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(INCORPORATED)

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Containing Papers and Discussions Presented at the Meeting Held in Birmingham, Ala., October, 1924, the Meeting Held in New York, February, 1925, and the Meeting of the Institute of Metals Division Held in Milwaukee, Wis., October, 1924

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PREFACE

In this volume are the papers and discussions presented at the Birmingham Meeting, October, 1924, the New York Meeting, February, 1925, and the Meeting of the Institute of Metals Division in Milwaukee, October, 1924; also the Proceedings of the Birmingham and New York Meetings.

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* Deceased. † Non-member at present.

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1923.	Gelasio Caetani	Rome, Italy.
1920.	Henry Sturgis Drinker	Merion Station, Pa.
1921.	Ferdinand Foch	Paris, France.
1922.	Federico Giolitti	Torino, Italy.
1888.	Haton de la Goupillière	Paris, France.
1906.	Sir Robert A. Hadfield	London, England.
1921.	Frank William Harbord	London, England.
1917.	Herbert Hoover	Washington, D. C.
1915.	James Furman Kemp	New York, N. Y.
1905.	Henri LeChatelier	Paris, France.
1921.	C. McDermid	London, England.
1913.	Ezequiel Ordonez	Mexico City, Mexico.
1909.	Alexandre Pourcel	Paris, France.
1911.	Robert H. Richards	Cambridge, Mass.
1907.	Charles D. Walcott	Washington, D. C.

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1872.	Sir Lowthian Bell	1904
1905.	Andrew Carnegie	1919
1892.	A. Del Castillo	1895
1902.	Manuel Maria Contreras	1902
1888.	A. Daubrée	1896
1906.	James Douglas	1918
1884.	Thomas M. Drown	1904
1890.	Moritz Gaetzschmann	1895
1873.	L. Gruner	1883
1921.	Heinrich O. Hofman	1924
1919.	Robert W. Hunt	1923
1891.	Bruno Kerl	1905
1895.	Joseph Le Conte	1901
1891.	J. P. Lesley	1903
1899.	Floris Osmond	1912
1890.	Adolph Patera	1890
1886.	John Percy	1889
1888.	Franz Posepny	1895
1911.	Rossiter W. Raymond	1918
1884.	Theodor Richter	1898
1899.	W. C. Roberts-Austen	1902
1890.	Albert Serlo	1898
1880.	C. William Siemens	1883
1906.	John E. Stead	1923
1909.	James M. Swank	1914
1872.	David Thomas	1882
1902.	Dimitry Constantin Tschernoff	1921
1873.	Peter R. von Tunner	1897
1885.	Hermann Wedding	1908
1910.	Tsunashiro Wada	1920

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PROCEEDINGS

Birmingham Meeting, 1924

THE 130th Meeting of the Institute was held at Birmingham, Ala., Oct. 13 to 15, with visits to other mines and districts. There were 71 members and guests on the special train from Washington; 55 from outside of Birmingham and 183 local members and guests made the total registration 309.

The party assembled at the New Willard Hotel, Washington, D. C., on the afternoon of Oct. 7. The men visited the Bureau of Standards and the Bureau of Mines; the women enjoyed an automobile sightseeing trip around Washington. In the evening a banquet was given by the Washington Section. George S. Rice, chief mining engineer of the Bureau of Mines, presented the Hon. Herbert Hoover as toastmaster; the speakers were President William Kelly and Past-President Arthur S. Dwight. The dinner was followed by dancing until midnight, when the party left on the special train for the South. The next day was spent in visiting the Luray Caverns and the Grottoes in the Shenandoah Valley.

Wednesday evening the special train arrived at Roanoke where a brief reception was held at the Hotel Roanoke and plans were outlined for the coal mines trip the following day. Edmund C. Pechin, one of the two living Founder Members of the Institute, resides within 20 miles of Roanoke but could not be present to greet the members. He is approaching his 90th year and, although in good health, could not attend the reception because it occurred in the evening. He would have done so, had it been held in the afternoon. Cordial greetings were sent to him by the members present.

Visit at Bluefield

Thursday found the party at Bluefield, W. Va., by invitation of the Pocahontas Operators Association. An illustrated booklet giving the geology and history of the Pocahontas district and a mile to mile itinerary of the 90-mile automobile trip through the coal fields, was distributed. In the booklet was an extract from the proceedings of the meeting of the Institute held in Roanoke, Va., in 1883, and a list of the members present at that meeting. John Graham, who was present at that meeting, was one of the hosts this year. Col. Edward O'Toole was a most excellent host at the U. S. Steel Corpn.'s headquarters at Gary.

Visit at Mascot and Copperhill

Mascot, Tenn., was reached on Friday morning, the 10th. The party alighted on the property of the American Zinc Co., where a large

tent served as an office for any requiring such service. A nicely printed program of the day and a visitor's card to the Cherokee Country Club were given to each member of the party, through the courtesy of J. H. N. Houser, general manager of the Tennessee Copper Co. The Tennessee Geological Survey had prepared and labeled for each member a package containing a marble bulletin, a zinc map, a state map, and a mineral map. The party was then conducted underground where the mining methods were explained by H. A. Coy, mine superintendent. A trip was made through the jig and flotation plants, after which the party was taken to Community Hall for luncheon. At each cover was placed a carton containing a bottle of white zinc oxide and one with jig and flotation tailings, souvenirs of the American Zinc Co.; also a black leather sack filled with Mascot lime, by the American Limestone Co., of Knoxville. Brief addresses of welcome were given by H. I. Young, the manager, and H. A. Coy; they were responded to by President Kelly and Arthur Thacher.

In the afternoon, the golfers were taken to the Country Club; the rest of the party were either taken on sightseeing trips through the city of Knoxville or to the various famous marble quarries within a radius of 15 or 20 miles and to the mill of the Knoxville Marble Co., where cutting and polishing the marble was shown and paper weights of polished marble were distributed.

In the evening, there was a formal dinner at the Whittle Springs Hotel. Col. William S. Shields, president of City National bank, was toastmaster. Director Frank Bane, of the Department of Public Welfare, welcomed the guests to the city. Other speakers were President William Kelly, Dr. Harcourt A. Morgan, president of the University of Tennessee; Past-President P. N. Moore, of St. Louis, and Wilbur Nelson, state geologist.

Saturday morning, the special train left Knoxville and arrived at Copperhill at noon. An attractive eight-page folder, describing the plant and operations to be visited, and a train schedule to the various places were distributed as the members of the party left their train for the special train of the Tennessee Copper Co., which took the party to the plant. Luncheon was served in the clubhouse of the Cowanee Club of the Tennessee Copper Co. At each cover was a large ash tray of T. C. Co. blister copper as a souvenir. J. N. Houser welcomed the party to Copperhill; his toast was responded to by President Kelly and E. F. Eurich, who told of the camp and plant as they were when he was employed here just after his graduation in 1866. After luncheon, the party visited the London shaft and flotation plant, then the McPherson shaft of the Burra Burra mine where some went underground while the rest visited the smelter and acid plant at Copperhill.

Chattanooga and Birmingham

Sunday morning, the party arrived in Chattanooga. The Engineers' Club of that city provided automobiles for trips to the battlefields at Lookout Mountain, Missionary Ridge, and Chicamauga and conveyed the party to the Signal Mountain Inn for luncheon.

Sunday night, the special train reached Birmingham. Very attractive and elaborate booklets, entitled "A Little Journey in the Birmingham District," and "Mining and Steel Making Methods in Alabama," published by the Tennessee Coal, Iron & Railroad Co., together with tickets for all the functions, were distributed to the members and guests as they registered.

Technical Sessions

Monday was devoted to technical sessions held at the meeting headquarters at the Tutwiler Hotel.

Morning Session

Chairman, George Gordon Crawford

Coal Washing Practice in Alabama. H. S. Geismer.
Byproduct Coking in Alabama. F. W. Miller.
Alabama Coal Mining Practice. Milton H. Fies.

Afternoon Session

Chairman, Frank H. Crockard

Blast-furnace Practice in Alabama. H. E. Mussey.
Steel Making in Alabama. James Bowron.
Production of Ferrophosphorus in the Electric Furnace. Theodore Swann.
Manufacture of Ferrophosphorus at Rockdale, Tenn. James A. Barr.
Manufacture of Cast-iron Pipe in the South. Richard Moldenke.

Evening Session

Chairman, T. H. Aldrich, Sr.

Economic Geology of the Birmingham District, Alabama. Ernest F. Burchard and Charles Butts.
Red Iron Ore Mining Methods in the Birmingham District. W. R. Crane.
Roof Support in the Red Ore Mines of the Birmingham District. W. R. Crane

Visits in the Birmingham District

Tuesday and Wednesday the entire party was taken by special trains, provided by the Alabama Mining Institute, to many of the mines and plants. A barbecue was given at Bayview by the Tennessee Coal, Iron & Railroad Co., and on Wednesday another was given at the Phoenix plant of the Phoenix Portland Cement Co.

Tuesday night there were two dinners at the Tutwiler. One was for those interested in the subject of industrial relations; the other was given by the Directors of the Institute and many younger members of the Institute were among the guests. At the latter, there was a general discussion of Institute affairs and concrete suggestions for progress. Following the dinners, in the Phillips High School Auditorium, the Colored Concert Choir of the Sixteenth Street Baptist Church rendered a program of southern songs in a dialect and manner new to the northern visitors. Moving pictures of the diversified interest and activities of the district were shown by the Alabama Power Co.

Wednesday night, a banquet and a dance were given at the Birmingham Country Club by the Alabama Mining Institute. George G. Crawford was toastmaster and his welcome to Birmingham was responded to by President William Kelly. The principal speaker of the evening was J. V. W. Reynders, first vice-president of the Institute.

John MacLeish, Director of Mines Branch, Department of Mines of Canada, was the last speaker; he voiced his appreciation of the Birmingham district and conveyed the felicitations of the Canadian Mining Institute, which he represented.

Thursday afternoon was spent inspecting the Wilson Dam and U. S. Nitrate Plant at Muscle Shoals.

Institute of Metals Division Meeting

THE annual joint meeting of the Institute of Metals Division and the American Foundrymen's Association was held at Milwaukee, Wis., Oct. 6–11. At the Non-ferrous Metals Session, the following papers were presented:

Casting and Heat Treatment of Some Aluminum-Copper-Magnesium Alloys. SAMUEL DANIELS, A. J. LYON, and J. B. JOHNSON.

Experiments on the Heat Treatment of Alpha-Beta Brass. O. W. ELLIS and D. A. SCHEMNITZ.

Coatings Formed on Corroded Metals and Alloys. GEORGE M. ENOS and ROBERT J. ANDERSON.

Hardness of Heat-treated Aluminum Bronze. GEORGE F. COMSTOCK.

New York Meeting, 1925

THE 131st meeting of the American Institute of Mining and Metallurgical Engineers was held in New York on Feb. 16 to 20, 1925, with a larger registration than at any previous meeting, the total being 1320.

Dr. John A. Mathews, of New York, delivered the Henry M. Howe Memorial lecture; the title of his lecture was "Austenite and Austenitic Steel."

Dr. Carl Benedicks, of Sweden, delivered the annual lecture of the Institute of Metals Division; the title of his lecture was "Studies on the Corrosion of Condenser Tubes with Special Reference to Hot-wall Action and Segregation."

Considerable interest was shown in the various symposiums. The annual symposium on petroleum is now looked forward to by all persons interested in oil and gas. The coal and coke symposium aroused so much discussion that an extra session was necessary for the presentation of the papers. At joint sessions with the Mining Section of the National Safety Council, under the auspices of the Industrial Relations Committee, rock dusting was discussed.

A joint meeting with the Mining and Metallurgical Society of America and the Mining Section of the National Safety Council was held.

The Committee on Mine Ventilation held its first meeting at which it discussed ways of attaining the purposes for which it was formed. Special luncheons and dinners were held by the Mining Methods Committee, which was followed by a general conference; Milling Methods Committee, Industrial Relations Committee, Iron and Steel Committee, and the Institute of Metals Division.

At the annual business meeting on Feb. 17, the following ticket was elected, and the reports of the President, Treasurer, and Secretary were presented:

J. V. W. Reynders, Director and President; John L. Agnew, Director and Vice-President; Ralph H. Sweetser, Director and Vice-President; Sydney H. Ball, Director; George D. Barron, Director; William H. Bassett, Director; J. M. Callow, Director; Charles F. Rand, Director.

E. De Golyer was elected First Vice-President; Charles F. Rand, Treasurer; Frederick F. Sharpless, Secretary; and Percy E. Barbour, Assistant Secretary, at the meeting of the Directors on Tuesday evening.

The Local Sections representatives met at 10 o'clock on Wednesday morning for the usual exchange of views regarding local section activities.

This meeting has become increasingly interesting and this year an extra session was held immediately after luncheon.

As usual a buffet luncheon was served each noon at the Institute Headquarters, members of the Woman's Auxiliary participating; these luncheons also were more largely attended so that the capacity of the fifth floor was severely taxed. Special luncheons and dinners were held by the Mining Methods Committee, Milling Methods Committee, Industrial Relations Committee, and the Institute of Metals Division.

On Monday afternoon a bronze tablet of Dr. Rossiter W. Raymond was unveiled in the lobby of the Engineering Societies Building, with appropriate ceremony.

The Annual Smoke was held in the Café Savarin, in the Pershing Building, on Monday evening. On Tuesday evening there was the usual informal dance at Institute Headquarters.

There were 727 guests at the Annual Banquet at the Waldorf, on Feb. 18, making this the largest banquet given at an Institute annual meeting. W. L. Saunders was toastmaster. B. B. Thayer, Chairman of the James Douglas Medal Committee, presented the name of William H. Bassett for the 1925 award of the James Douglas gold medal, and J. V. W. Reynders, President of the Institute, presented the medal and diploma. Addresses were made by William Kelly, retiring President; Hon. Charles McCrea, Minister of Mines for the Province of Ontario, Canada; Maj.-Gen. Charles P. Summerall, Commanding Second Corps Area, which includes New York; and J. V. W. Reynders, the new President.

On Thursday, more than 300 members and guests went by special train to the Naval Air Station at Lakehurst, N. J. Naval officers were in attendance to explain the station and ships. A luncheon was served in the Air Station theater, following which Dr. R. B. Moore gave a brief talk on helium, its method of recovery, and repurification.

On Friday, at the invitation of President C. W. Nichols, the nonferrous metallurgical group visited the metallurgical plant of the Nichols Copper Co. at Laurel Hill, L. I. After examining the plant the members were entertained at luncheon by the plant officials.

The Woman's Auxiliary had its usually very full and interesting program for each day of the meeting.

Technical Sessions

Institute of Metals Division

George K. Elliott, Chairman

New Developments in High-strength Aluminum Alloys. Robert S. Archer and Zay Jeffries.

Etching Aluminum and Its Alloys for Macroscopic and Microscopic Examination. Fulton B. Flick.

Scratch and Brinell Hardness of Severely Cold-rolled Metals. M. F. FOGLER and E. J. QUINN.
Eutectic Patterns in Metallic Alloys. C. H. GREEN.

WM. M. CORSE, Chairman

X-Ray Evidence versus the Amorphous Metal Hypothesis. ROBERT J. ANDERSON. and JOHN T. NORTON.
The Malleability of Nickel. PAUL D. MERICA and R. G. WALTENBERG.
Recrystallization and Grain Growth in Soft Metals. MAURICE COOK and ULICK R. EVANS.
Determination of Structural Composition of Alloys by a Metallographic Planimeter. E. P. POLUSHKIN.

GEORGE C. STONE Chairman

Corrosion of Copper Alloys in Sea Water. WILLIAM H. BASSETT and C. H. DAVIS.
Tantalum, Tungsten and Molybdenum. E. W. ENGLE.

Coal and Coke Symposium

DAVID WHITE, Chairman

Environmental Conditions of Deposition of Coal. DAVID WHITE.
Microscopical Constitution of Coal. REINHARDT THIESSEN.
Microstructure of Coal. CLARENCE A. SEYLER.
Microscopical Structure of Anthracite. HOMER G. TURNER.
Coal in Relation to Coke. EDWARD C. JEFFREY.
The Resolution of Coal by Oxidation. W. FRANCIS and R. V. WHEELER.
Constitution of Coal. F. V. TIDESWELL and R. V. WHEELER.
Organic Sulfur Compounds in Coal. J. JOLLY and R. V. WHEELER.
Selective Combustion in Coal. F. S. SINNATT.
Nitrogenous Constituents of Coal. JOHN W. COBB.
Coal and Oxygen. SAMUEL WILSON PARR and F. B. HOBART.
A Modern View of the Chemistry of Coals of Different Ranks as Agglomerates. ARNO CARL FIELDNER and J. D. DAVIS.
Contact Metamorphism of Some Colorado Coals by Intrusives. J. BRIAN EBY.
The Progressive Regional Carbonization of Coal. DAVID WHITE.
Moisture as a Component of Volatile Matter of Coal. WILLIAM TAYLOR THOM, JR.

Petroleum

E. DE GOLYER, Chairman

Conservation of Oil. HENRY L. DOHERTY.
World Production of Petroleum in 1924. E. DE GOLYER.
Bearing of Price on Oil Reserves. JOSEPH E. POGUE.
Ratio of Peak Production to Estimated Total Production in Certain Oil Fields. G. B. RICHARDSON.
First Test of the Clinton Oil Sand in West Virginia. DAVID B. REGER.
Value of Aerial Photographic Surveying and Mapping to Petroleum Companies. H. CASE WILLCOX.

Aerial Photographic Maps. Gerard H. Matthes.
Development during 1924 in:
- Pennsylvania and New York. Meredith E. Johnson.
- West Virginia. David B. Reger.
- Ohio. J. A. Bownocker.
- Kentucky and Tennessee. Wilbur A. Nelson.
- Indiana. W. N. Logan.
- Illinois. G. F. Moulton.
- Gulf Coast. David Donoghue.
- Texas Outside of the Gulf Coast District. F. H. Lahee.
- Oklahoma. R. S. McFarland.
- Kansas. Everett Carpenter.
- Montana. Max Bauer.
- Wyoming. E. L. Estabrook.
- Colorado. C. H. Wegemann.
- Mexico. Valentin R. Garfias and R. V. Whetsel.
- Venezuela. Edwin B. Hopkins and H. J. Wasson.
- Peru. V. F. Marsters.
- Colombia. L. G. Huntley.
- France. P. Martignan.
- Poland. Leon Orlowski.
- Rumania. George Anagnostache.
- Canada. G. S. Hume.
- Russia. A. Beeby Thompson.
- Cuba. Ralph Arnold.

The Jurassic as a Source of Oil in Western Cuba. Albert Wright, Jr., and P. W. K. Sweet.
Increasing Production of Petroleum by Increasing Diameter of Wells. Lester C. Uren.
Significance of Fluid Level in Oil Well Pumping. Lester C. Uren.

Mining Methods—Metal

R. M. Raymond, Chairman

Methods of Mining and Ore Estimation at Lucky Tiger Mine, Sonora, Mexico. R. T. Mishler and L. R. Budrow.
Mining Methods of Jarbidge District, Nevada. John Park.
Mining Methods at Cornucopia, Oregon. Robert M. Betts.
Mining Methods in Zaruma District, Ecuador. Rudolph M. Emmel.
Mining Methods at the Homestake. A. J. M. Ross and R. G. Wayland.

Mining Methods—Coal

Thomas H. Clagett, Chairman

Systems of Coal Mining in Western Washington. Simon H. Ash.
Method of Mining a Steeply Pitching Anthracite Vein by Successive Skips. J. S. Miller.
Simultaneous First and Second Mining on Steep Pitches. Dever C. Ashmead.
New Orient, an Unusual Coal Mine. George B. Harrington.
Properties of Liquid Oxygen Explosives. G. St. J. Perrott.

Coal

C. M. LINGLE, Chairman

Ultimate Recovery from Anthracite Beds. HENRY H. OTTO.
Schedule Rating Coal Mines in Pennsylvania for Compensation Insurance Rates. RUSH N. HOSLER.
Application of Gaussian Curves to Mining Industry. HUGH ARCHBALD.

Joint Meeting Coal and Petroleum

S. A. TAYLOR, Chairman

Safeguarding Coal Mining Operations against Danger from Oil and Gas Wells. A. W. HESSE.
Belt Conveying of Coal, H. C. Frick Coke Co. Mines. Illustrated with Motion Pictures. THOMAS W. DAWSON.
Analysis of the Performance of the Coal Jig. H. F. YANCEY and THOMAS FRASER.

Ground Movement and Subsidence

LOUIS S. CATES, Chairman

Factors Affecting Bank Slopes in Steam-shovel Operations. LOUIS S. CATES.
Mine Support and Mine Subsidence in the Birmingham Districts. W. R. CRANE.
Rock Bursts and Bumps. GEORGE S. RICE.

Non-metallic Minerals

HEINRICH RIES, Chairman

Limestone Production as a Mining Problem. J. R. THOENEN.
Engineering in Limestone Production. C. C. GRIGGS.
Manufacturing Problems of Cement Industry. JOHN J. PORTER.
Rotary Calciners for Gypsum. FRANK A. WILDER.
Phosphate Deposits of Idaho and Their Relation to the World Supply. VIRGIL R. R. KIRKHAM.

Milling Methods

CHARLES E. LOCKE, Chairman

Recent Developments in Fine Grinding and Treatment of Witwatersrand Ores. CARL R. DAVIS, J. L. WILLEY, and S. E. T. EWING.
Determination of Dissolved Oxygen in Cyanide Solutions. A. J. WEINIG and MAX W. BOWEN.
Precipitation Efficiency of Zinc Dust in Cyanide Process. ROBERT LEPSOE.
Studies on the Precipitation of Gold and Silver on Charcoal from Cyanide Solution. JOHN GROSS and J. WALTER SCOTT.

Non-ferrous Metallurgy

E. P. MATHEWSON, Chairman

Redistillation of Zinc. KURT STOCK.
High Zinc in Lead Blast Furnace Slags. FRED E. BEASLEY.

A New Roasting Furnace for Zinc Flotation Concentrate. CHARLES H. FULTON and J. BURNS READ.
Application of Pulverized Coal to Copper Refinery Furnaces. E. W. STEELE.
Recovery of Arsenic and Other Valuable Constituents from Speiss. C. P. LINVILLE.

Iron and Steel

R. H. SWEETSER, Chairman

Manganiferous Iron Ores of Cuyuna District, Minnesota. CARL ZAPFFE.
Economics of the Cuyuna Manganiferous Iron Ores. C. P. McCORMACK.
Probable Error in Blast Furnace Records and Calculations Therefrom. T. T. READ.
Reduction of Iron Ores by Carbon Monoxide. HEIHACHI KAMURA.
Effect of Sulfur on Blast Furnace Process. T. L. JOSEPH.

ALBERT SAUVEUR, Chairman

Chemical Equilibria during Solidification and Cooling of White Cast Iron. H. A. SCHWARTZ and (Mrs.) ANNA NICHOLSON HIRD.
Some Factors Affecting the Elimination of Sulfur in the Basic Open Hearth Process. C. H. HERTY, JR., A. R. BELYEA, E. H. BURKART, and C. C. MILLER.
Finishing Melting Temperatures of Simple Ingot Steels. HENRY D. HIBBARD.
The Reaction between Manganese and Iron Sulfide. C. H. HERTY, JR. and O. S. TRUE.
Brief History of Metallurgical Practice in Cannon Making with Particular Reference to the Cast Iron Gun. JOB GOOSTRAY, R. F. HARRINGTON, and M. A. HOSMER.

Joint Session with the Mining Section of the National Safety Council

Prevention of Coal-dust Explosions

BENJAMIN F. TILLSON, Chairman

Review of Coal Dust Investigations. GEORGE S. RICE.
Economics of Rock Dusting Bituminous Coal Mines. EDWARD STEIDLE.
Determination of Suspensoids by Alternating Current Precipitators. PHILIP DRINKER, and R. M. THOMSON.
Value of Humidifying Methods in Explosion Prevention in Coal Mines. DANIEL HARRINGTON.
American Recommended Practice for Rock Dusting Specifications: Report of Sub-Committee of the Mining Correlating Committee on Rock Dusting. E. A. HOLBROOK.
Silicosis and Its Prevention, Illustrated with the film, "The Dust That Kills." R. R. SAYERS.

Joint Session with National Safety Council and Mining and Metallurgical Society of America, under the Auspices of Industrial Relations Committee

R. M. CATLIN, Chairman

Maintaining Interest in Safety. C. B. AUEL.
Essential Factors of Industrial Relations. C. F. DIETZ.

PAPERS

Environmental Conditions of Deposition of Coal

By David White, D.S.,* Washington, D. C.

(New York Meeting, February, 1925)

The environmental conditions under which coals are deposited are revealed by the stratigraphy of the coal basins and coal beds and by the details of the structure and the physical constitution of the coals themselves.

The Land Surface

Generally Low Relief or Base Level

In the Paleozoic coal fields, which have longest been worked, are most important, and are best known, we find relations, in general, as follows: A post-Mississippian uplift with, in most cases, very moderate deformation, followed by erosion by which the uplifted regions, especially the bolder of the new topography, were largely worn down, while the older and less deformed regions were more or less extensively base leveled. Base leveling of most of the region continued as the deposition of coal measures proceeded. Consequently, in most coal fields the Pennsylvanian, or upper Carboniferous, lies unconformably on the Mississippian or on older formations. There are but few regions in which sedimentation is seen to have been apparently continuous from the Mississippian into the Pennsylvanian "Coal Measures."

Axis of Greatest Subsidence Flanks Axis of Upwarp

In most regions the initial deposition of "Coal Measures" took place in a narrow trough lying at the foot of and parallel to an axis of post-Mississippian uplift. The early "Coal Measures" deposits consist largely of sand with conglomerate, sometimes in great amounts, derived from the upwarping area. Generally, only fresh- or brackish-water deposits are found over the greater part of these initial basins, most of which are in the form of long narrow estuaries, or elongated fluviatile and lacustrine basins.

Expansion of Early Basins

In every case, there is evidence of filling of the early narrow basin, with lateral extension of the area of sedimentation; but it is to be noticed

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that the encroachment was relatively restricted on the side toward the uplifting axis, though this is the side of deposition in greatest thickness, both because most of the clastic sedimentary material was derived from this side and because the greatest subsidence or depression of the trough occurred here. Meanwhile the axial land mass itself was in most cases uplifted in intermittent or irregular movements of slight or minor magnitude. On the opposite side of the basin, the surface of the "Coal Measures" sediments extended farther and farther inward over the opposite lowland coast. Thus, a broadening area, including as its eccentric focus the initial basin, was subsiding and being filled, usually with some warping of the underlying land mass, as the area of sedimentation encroached farther and farther on the base-leveled region of the continental mass, or across the lowlands and marshes of the fresh-water basin. Normally, this continued until toward the close of coal-measures deposition, when incipient deformation took place, with the development of new areas of uplift and restriction of the areas of sedimentation—movements that, in most cases, were more or less unfavorable for the deposition of coals. The movements appear to have been isostatic.

The progressive steps in the development of the typical "Coal Measures" basin just outlined are seen in most European as well as in American coal fields. In the Appalachian region, the comparatively narrow trough of early Pennsylvanian (lower Pottsville) deposition lies at the eastern margin, including the Coosa and Cahaba basins in Alabama. The easternmost tip of the Pocahontas region is dipping down from the west into the basin, while Pottsville, Pennsylvania, is apparently well down toward the bottom on the western slope of the early trough. Likewise, in the mid-continent region, the earliest "Coal Measures" of Texas flank the Llanorian uplift, on the east, and the tremendous thickness of Pennsylvanian in Arkansas and Oklahoma lies in the early Ouachita axis on the north of Llanoria. Here the early "Coal Measures" deposition gradually encroached farther to the north and, in late Pottsville time, a comparatively narrow estuary or valley extended from the region embracing Vinita and Bartlesville, Okla., northeastward across southeastern Kansas and northwestern Missouri into Iowa, where it apparently shoaled out broadly. The deposits of latest Pottsville age embracing the Bartlesville oil sands in this basin, were probably derived from the now buried Nemaha Mountains. The Paleozoic coals of the Rocky Mountain region were similarly laid down along the flanks of the post-Mississippian uplifts.

Unstable Level

The great variability in the composition of the "Coal Measures" sediments, which range from coals, fine silts, and limestones through sandy shales, shaly sandstones, and sandstone to coarse conglomerates, which often seem irregularly distributed in the vertical column, reflects

and proves the instability of the continental region in which they were laid down and, in particular, of the land mass whence the sediments of terrestrial origin were largely derived. The occasional presence of limestones and other deposits carrying marine fossils, which occur here and there between other beds carrying brackish- or even fresh-water fossils, unmistakably proves either fluctuation of the sea level (that is, rising and falling of the land), or exclusion of the sea at times as the result of tilting of the regions or the formation of barriers. Generally it is the former. Both causes have operated in different regions and, at different times, in the same region. It is, however, to be noted that the seas which invaded the early narrow estuaries or spread out over the broad flood plains and base-leveled regions were never deep. Probably, in most of our large coal fields the surface of sedimentation seldom or never lay as much as 200 ft. below tide level, and then only for intervals. Much of the time, on the other hand (at least during the times of deposition of coals of commercial purity) the sea was excluded from the region of coal formation.

Contemporaneous Erosion Common

Under the conditions prevailing, the occasional erosion of newly formed sandstones, shales, or coals in consequence of exposure or slight local or regional deformation was normal, as also were the consequent local unconformities and the deposition of heavy outwash sandstones or conglomerates as the result of elevation of the sources of supply and acceleration of the drainage flowing into the basin. It was under precisely such conditions that the Mahoning sandstone, which over considerable areas is somewhat conglomeratic, was laid down; the Homewood sandstone, which marked a change in the elevation of the shore regions as well as slight differential movement in the interior of the basin; or the Sharon conglomerate, the Raleigh sandstone, etc. The Raleigh sandstone, which lies at the base of the middle Pottsville, is restricted to a relatively narrow zone in and bordering the axial basin of early Pottsville deposition. Analogous conditions prevail in the mid-continent and southwestern regions.

Invasions of the Sea

Most, if not all of the limestones of the lower Conemaugh and older Pennsylvanian formations of the Appalachian trough, and apparently all of the limestones in the interior and western "Coal Measures" basins are definitely marine, though many of them bear evidence of having been laid down nearly up to tide level, with very shallow covering of water. This is proved by wave and ripple effects, by the earthy material included in many of them, by the character of their contacts, by the occasional presence of vascular plants rooted in hollows and crevices, and, very rarely, by the development of soils that in some places lie immedi-

ately on the surface of the thin limestones, as is described by Hinds and Green.[1] Some of the thin earthy limestones are mud-cracked. Sometimes the transition from the marine bed, especially a limestone bed, to the Stigmaria underclay is abrupt; more often shales and sandstones intervene. Frequently, the "underclay" beneath the coal lies on sandstone, though prevailingly it lies on shales. Very rarely it lies, with slight intercalation of carbonaceous mud, on another coal.

The Swamp Environment

Freshwater Swamps the Site of Ordinary (Woody) Coal Formation

The typical Stigmaria clay that almost invariably underlies the Paleozoic coal is familiar alike to the engineer and geologist, who usually style it erroneously as fireclay. The innumerable rootlets and the larger roots of Stigmaria are nearly always conspicuous or may be readily found in these clays though, on account of lack of close attention, the obvious evidence of growth in place is not so commonly noted. The miners are apt to identify the larger roots as "snakes," in which case, naturally, rootlets and growth in place are not looked for.

Old Soils under Coal Beds

Careful observation of the underclays beneath different coals and in different regions shows not only that the Stigmariæ are generally in place of growth,[2] but that the underclays occasionally embrace debris of land plants that have become covered in the course of deposition. Roots of ferns or cycadofilic trunks, also in place of growth, are common and, where sandy, Calamarian types; for the Calamarian group always grew in wet soil, some of the types favoring wet sands, just as do most of the living Equiseta of the present day.

The building up of the underclay by further sedimentation under a very thin, and probably fluctuating, water cover often took place, in which cases root systems developed at successively higher levels from the larger plants, as was shown by Grand'Eury.[3] Marine fossils are not found in the typical underclay and even brackish-water fossils are practically unknown except in very rare occurrences of carbonaceous "slate" or somewhat bony black stuff between the pure coal and the underclay.

The typical underclay is now known to be an old soil formed in a swamp. Its upper portion, at least, is non-marine and non-brackish; it is terrestrial and was, at times, subaerial; that is, exposed land.

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[1] H. Hinds and F. C. Green: The Pennsylvanian of Missouri: *Report* Missouri Bur. of Mines and Geol. (1915).

[2] J. J. Stephenson: *Proc.* Amer. Phil. Soc. (1916) 21; (1917) 53; (1918) 1.

[3] F. C. Grand'Eury: Recherches Géobotaniques sur les Forêts et Sols Fossiles, etc., pts. I-III (1912-1914).

Water in Swamps

The nearly omnipresent Stigmariæ are the rhizomes and roots of different types of the giant Paleozoic lycopods of the groups Sigillaria, Lepidodendron, Bothrodendron, Lepidophloios, etc., which were the dominant trees of the Carboniferous swamp forests. These trees were adapted to growing in swamps in which a shallow cover of water was normally present, very much as in our southern Atlantic coast swamps, during the larger part, at least, of the year.[4] The roots, by their spread near the surface, their organization or structure, and the characters of their rootlets, such as air chambers and the absence of root hairs, were adapted to growing flatwise near the surface of the mud in a wet swamp. Some of the Stigmariæ had "knees" similar in development and disposition to those seen in the bald cypress growing in the water-covered swamps of our Southern States. Both knees and trunks were provided with hydathodes and pneumatophores to regulate water content and furnish air supply to the roots. Further, the bases of the trunks of the common Sigillaria and Lepidodendron were dilated abruptly for two or three feet above the roots and were provided with special structural features, just as are the gums and cypress trunks occurring in the water-covered swamps of the present time. The dilations mark the ordinary water level in the swamp. These features have been strikingly illustrated by Potonie.[5] The rootlets of the fern trunk contained gum canals, and the Calamarian roots had air spaces; all indicative of an aqueous habitat.

Most of the giant lycopods of the early and middle "Coal Measures" were heterosporous; that is, they bore two types of spores, one large and one small, of different sexes. These spores, as will be pointed out later, were provided with thick resinoid or waxy-resinous outer envelopes (exines) to prevent decay in water, and the perpetuation of the species was largely dependent on the water cover of the swamp to drift megaspore and microspore into conjunction.

In fact, it will be seen that when, due to climatic changes, the persistence of the water cover in the swamps became too uncertain the giant lycopods waned and soon disappeared, other types of trees, verging into the orders of coniferous gymnosperms, and giant tree ferns taking their places.

Swamps Generally Forest Covered

The typical coal bed, of commercial purity, laminated and of wide extent, is only a compressed, reduced, lithified, and more or less altered peat. Not only is it a swamp deposit, as illustrated by Doctor Thiessen,[6]

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[4] D. White: The Carbonaceous Sediments; in Treatise on Sedimentation, by W. H. Twenhofel and others; MS. is in hands of editor.

[5] H. Potonie: Entstehung der Steinkohle (1920) 6th ed., 118, 188.

[6] Microscopical Constitution of coal; see p. 35.

but it is distinctly a fresh-water swamp deposit. Both the plants from whose debris the coal is formed, as shown by the microscopical study of the fuels, and the fossil plants associated with the coal beds (those found in the shales or sandstones immediately overlying the coal and those present in the clay partings within the coal bed itself) are land plants, vascular, and more or less woody in composition, belonging to the Pteridophytes and higher orders of plant life. In general, they grew on or near the spot where their debris is found. Those accompanying and composing the coal in the exclusively fresh-water basin are indistinguishable from those accompanying coals not only in the fresh-water zones of formations carrying marine horizons, but even in measures where the underclays and overlying coals are intercalated in series distinctly marine; as in Missouri where, extremely rarely, limestones lie immediately beneath the underclay, and marine fossils mingle with fossil-plant debris in the roof shales. Similar relations between the coal and fossiliferous marine beds may be found locally at the level of the Ames limestone or in the Mercer shale in western Pennsylvania.

Plants Forming Ordinary Coals Not Halophytic

The typical coal-forming vegetation did not and could not live in salt or brackish water. No vascular plant forms have yet been recognized as distinctive of the coal deposits laid down in areas of proximity to sea level, like the Eastern Interior coal field where temporary subsidence of the land or the breaching of bars, such as invariably characterize the borders of a subsiding base level coast, so often permitted the sea to overwhelm and kill the coal-forming swamp vegetation. The features of the underclay, the plants forming the coals, the bedding and even the lamination of the coals reveal no appreciable or essential distinction between the coals of the distinctly fresh-water basins and those laid down in the great lowland swamps of areas like the Illinois-Indiana and the Missouri-Kansas fields, where proximity to sea level and instability of land elevation permitted the exposure of great expanses of sea bottom, and the development thereon of swamps and land floras. The deposition of coals was usually followed by some thickness of non-marine shales and sandstones, before a too rapid rate of subsidence again made possible the reinvasion of salt or brackish water over the coal-forming swamps. So far as I have been able to learn, coals (peats) of ordinary woody type and of commercial purity and of great horizontal extent are not now being laid down in brackish or salt water in any part of the world.

Salt-water Invasions of the Swamps

In some regions, salt-water invasions occurred in the midst of coal formation (peat deposition) in portions of the tide-level swamps of Missouri and Illinois, as is shown by the presence of debris of marine mollusks

in thin partings occurring locally within the coal beds. Not infrequently, also, one may observe the presence of roots of land plants that grew in place in the marine muds of the partings, as in most cases these invasions may have resulted from breaching of barrier beaches. I have, in earlier papers,[7] emphasized the part played by such barriers in some of the tide-level coal fields like those of the mid-continent and interior areas, and the probable effectiveness of the dense vegetable growth in obstructing the progress of salt water into the swamp. In other cases, it is likely that the advance of salt water would be checked also by low gradients of the swamp as it spread across the somewhat uneven surface. Irregularity of this surface is, in many instances, indicated by the varying floor and thickness and bedding of the coal beds.

Muck in Coals

In the Illinois and Indiana coal fields, some of the coals, especially Nos. 3, 5, and 6, are covered, over large areas at least, by mucky carbonaceous material more or less laminated and frequently marked by very thin intercalations—sometimes mere films—of inwashed sand. Here, the surface of the peat swamp has been partly oxidized after denudation of its vegetal cover, and some of the peaty substance, reduced to muck, has been relaid under wave action with thin washes of sand. Marine fossils occur here and there in these deposits, in which delicate parts of plants, such as fern leaves, are generally wanting; due probably to attrition, slowness or instability of deposition, and the greater opportunities for oxidation.

Rise of Water Level

In any coal bed, the principal changes in structure and constitution are due to changes in the water level. In most regions, rise of the water level ran more or less nearly parallel to the growth in thickness of the peat deposit; for bituminous coals as much as 6 or 7 ft. thick this thickness must originally have been over 40 or 50 ft. This predicates a gradual sinking of the tide-level swamps as the surface of the peat was built up, and explains how readily a slightly too rapid subsidence, with or without consequent breaching of barrier sands, might permit salt-water invasion and, with continuous subsidence, the coals could be overlain by marine muds, shales, or limestones. Elevation of some part of the higher land or the receipt of larger contributions from some sand-lain area, might cause the deposition of sandstone. Filling the basin caused readjustment of the surface of sedimentation; and, if the water level rose too little, even as raised by the peat itself, vegetal accumulation suffered more advanced decay and peat formation was slower or its growth was arrested.[8]

[7] D. White and R. Thiessen: Bur. of Mines *Bull.* 38 (1913) 52.

[8] D. White: The Carbonaceous Sediments (1923).

Sulfur and Silicification

In earlier papers, I have emphasized the generally far greater amounts of sulfides in the tide-level basins, a relation that is quite generally recognized, though the assumption that the larger sulfur supply has to do with the sulfur of the marine animal life rather than with reactions in the salts of the marine or brackish waters impregnating beds not far distant above or below the coal invites more thorough consideration by the chemist.

In the fresh-water basin, which is fluviatile or shallowly lacustrine, the interruption of peat formation by too deep inundation, with more or less extensive inwashing of silts, sand, etc., thus burying the peat deposits, affords conditions much more favorable for the preservation of the remains of the land vegetation growing on the swamp. The flora is overwhelmed and buried or slowly drowned out while sedimentation is in progress, instead of being exterminated by the salinity of encroaching sea water.

The apparently sudden segregative precipitation of colloidal silica at or close to the surface of the organic deposits, so as to form siliceous nodules or to cause the partial impregnation of logs, stems, fruits, etc., is, in most cases at least, almost certainly due to rapid invasions of saline or brackish water. With the siliceous segregations, pyrite or marcasite is apt to occur. This explanation is consistent with the occurrence of such nodules and impregnations in what we commonly call marine coal measures basins, like those of the interior and mid-continent regions—that is, in the tide-level swamps. The impregnation of the vegetation by silica or lime occurred unmistakably at the time of, or very soon after, deposition.

Similar Conditions in Mesozoic and Tertiary Coal Fields

The depositional relations of the Mesozoic and Tertiary coal fields of the western United States were, in general, evidently similar to those of the Paleozoic areas with respect to the topography. Most of the western basins were far less extensive than the eastern Paleozoic lowlands, and some of them appear to have been relatively restricted, but the coals were nevertheless laid down in lowlands and marginal swamps that crept upward on a gradient too low to permit drainage under the climatic conditions prevailing, and whose level was raised and broadened by growth of peat and rise of the water level.

The coal measures were deposited in fresh-water basins, in estuaries, and in broad coastal swamps generally bordering epicontinental seas. Shifting of shore lines or accentuation of erosion, presumably consequent to uplift or deformation of the source regions of the arenaceous sediments, is recorded in the wedge shapes or lenticularity of the sandstones and the tongue characters of those coal measures groups, which represent conti-

nental deposits fingering into the marine sediments of the epicontinental sea. This is particularly true of the Cretaceous coal measures of the Mesaverde in Montana, Wyoming, Colorado, and New Mexico.

Examination of the floras of the coal beds in the principal western coal fields nearly everywhere discloses the existence of old soils with roots beneath the coal beds. The roots, which are clearly seen to be in position of growth, are rather more varied in botanical range than in the Paleozoic, where Stigmaria is so omnipresent. In some areas shallow basins, lakes, or ponds evidently were in process of filling until land vegetation was able gradually to spread out from the edges so as to cover the surface, which eventually was forested exactly as is to be seen in many peat swamps at the present time. In these cases, carbonaceous muds and shales underlie the purer, well-bedded, laminated coals, which in general are characteristically woody. The occasional influx of oversweeping and aggrading muds and sands, burying the swamps so as to cause partings in the coal beds or even the total suspension of coal deposition for considerable time, harmonizes with the now more generally recognized instability of the continental masses and the generally fluviatile sedimentation of the fresh-water basins in which, however, lakes unmistakably were present.

Climatic Conditions of Coal Formation

The study of both the structures of the coal bed and the microscopical constitution of the coal itself confirms the evidence of the stratigraphy and the sedimentation of the enveloping strata in proof that the coals of the normal types (whether lignite, bituminous, subbituminous, or anthracite) were laid down as peats, most of the deposits of common type having been formed in forested swamps of great extent. As at the present time, the environment of peat formation varied somewhat, but the ordinary woody coals were certainly laid down on broad coastal plain or inland swamps covered more or less of the time by water, which during peat deposition, however, was not so deep as permanently to interrupt the growth of arborescent vegetation.

Sunlight and Wind

Comparison of the structural features of the coal-forming vegetation of the Tertiary and Upper Cretaceous with moist lowland and swamp trees, shrubs, and ferns of the present day leaves no room for doubt that the overhead conditions as to sunlight and clouds, with wind, were in general comparable to those of the moderately humid and very humid regions of the earth at the present time. The immediate ancestors of the bald cypress were present in most Tertiary coal swamps. Winged seeds indicating dispersing winds were common.

The features of the vegetation that grew in the Paleozoic swamps similarly indicate sunlight, probably in moderate amount, while ripple marks and, in some cases, fairly well-developed wave marks in the coal measures strata bear testimony as to winds. Many of the Carboniferous seeds and fruits were provided with wings to assist in distribution.

Rainfall and Temperature

An inspection of the evidence as to humidity and rainfall shows some variation, not only from region to region, but from period to period in the same regions. The deposition of Paleozoic peat in the enormous thicknesses required to form workable coal beds, as the deposits are now reduced, calls for a climate more or less distinctly humid or even wet. In most regions, the rainfall was either moderately heavy and well distributed through the year or it was copious through the greater part of the year.[9]

Lower Pennsylvanian

In the Pottsville coal measures of North America and in the Westphalian series of Europe, which is nearly equivalent in age, the evidence clearly points toward abundant rainfall relatively well distributed throughout the year. General humidity, as well as mildness of temperature, is shown by the rapid and large growth of the lush vegetation. The Pottsville and lower Alleghany plants, in particular, had large and comparatively thin-walled cells with large intercellular spaces. The digestive tissue of the leaves was conspicuously lacunose, and provision was made for discharge of excess of water content of many of the plants. The lycopods and Calamariæ, the latter being related to the living horsetails, were gigantic and the ferns and fernlike cycadofilic types were mostly very large or greatly elongated. The pose of branches and leaves and the leaf forms suggest the shedding of rain. Most of the fernlike types of the genus Sphenopteris, especially those included by Stur in his genus Diplothmema, were long clambering plants, probably climbing on to or over the more robust types, such as Neuropteris and Alethopteris, which were themselves small trees, the trunks of which attained in some cases a diameter of nearly two feet. Many of these clambering or climbing plants of the Pottsville, and particularly the New River and the Kanawha divisions of the Pottsville, had very delicate, even membranaceous, foliage—filmy, and often deeply dissected. Rhacophyllum, by its

[9] E. Carthaus: Die Klimatischen Verhältnisse der geologischen Vorzeit von Präcambrium bis zur Jetztzeit, 1910; A. G. Seward: Climate as Tested by Fossil Plants, 1914; A. G. Nathorst: Smithsonian Report, 1911; W. Gothan: Die Jahresringlösigkeit der pälaozoischen Baüme, 1911; P. Bertrand: *Ann.* Soc. Géol. Nord, (1909) **38**, 92; C. Schuchert: Smithsonian Report, 1914; H. Carpentier: Les plantes fossiles. *Rev. Gén. Bot.*, 1922; D. White: Bur. of Mines *Bull.* 38 (1913), and The Carbonaceous Sediments.

habit, and some of the ferns, by the distribution of their nearest living relatives, are connected with warm climate floras. At this time, the forests of the American and western European coal fields were truly subtropical or tropical in aspect. A very mild, or, at least, subtropical, temperature is shown not only by the enormously rapid growth and the delicacy of the fernlike lianas, but it is indicated further by the absence, or only very slight development, of rings of annual growth. Growth of plants during these periods appears to have been almost free from interruption and certainly free from severe winter frosts in temperate latitudes.

Some instability of the water level in the swamps is shown by the bedding and lamination, including the layering of "mother of coal," to which reference will later be made, but the general maintenance of a thin water cover over the surface of the swamps during the great part, at least, of the year is shown by the dilation of the basal 2 or 2½ ft. of the butts of many of the trees, and by the presence of knees, by pneumatophores, etc. Many of the seeds and fruits were provided with air chambers to aid flotation. Closure of pollen chambers prevented entrance of water pending delayed pollination of the ovules in some of the genera. Reference has already been made to the prevalence in this period of heterosporous lycopods, the continuation of whose species required an aquatic environment in which the megaspores and microspores might drift into conjunction. Low herbaceous types seem to have been exceedingly rare. Mosses are almost unknown.[10]

Upper Pennsylvanian Time

In the upper Pennsylvanian, which includes the upper Alleghany, the Conemaugh, and the Monongahela coal measures in America and the Stephanian of Europe, the climate appears to have been less uniform. The rainfall was apparently less evenly distributed through the year and the humid subtropical or tropical lianas are less in evidence. This is particularly true of the Appalachian coal fields, where tree ferns are far more numerous and varied. The changes may be connected with the causes of the introduction of red beds deposition in this region. In the tree ferns and in some of the lycopods, we have immensely thickened bark (including internal ramenta) with structural physiological provision for water storage, presumably to tide over seasons of reduced rainfall. The probable occurrence of dry seasons is further shown by the rapid disappearance of the heterosporous lycopods, whose dominance called for a greater persistence of the water cover in the swamps. Most of the membranaceous types had disappeared or were disappearing. The cycadofilics had larger pinnules and lobes, and the leaflets of the Pecopterids and other tree ferns were prevailingly not only rather thick but more or less villous. The ecological characteristics were accordingly comparable

[10] D. White: Bur. of Mines *Bull.* 38 (1913) 74.

to a subtropical or mild tropical dense plant growth with abundant tree ferns all adapted to a short dry season, although the total rainfall was relatively large. Ample precipitation or water cover is, however, requisite for peat formation in tropical regions.

Consistent with the postulated conditions, wood growth appears to have been rather less rapid than in the earlier coal measures, and the cells are generally rather thicker, and, what is more significant, the wood in some of the types has more or less well-developed annual rings. The general character of the vegetation, which included many genera whose present-day representatives are distinctly tropical or subtropical, justifies the conclusion that the growth rings, which neither in western Europe nor in eastern America are as well defined as in the regions of present-day winter frosts, probably reflect merely the interruption of growth by dry seasons rather than by severe winter freezing.

Permian Climate

Seasonal changes are still more evident in the Permian deposits—even those laid down in the generally moist regions of coal formation. Fluctuation in rainfall is fairly evident and, outside of coal field areas, xerophytic plants are not rare. In the United States, the evidence as to alternating wet and dry seasons in the Permian may be regarded as conclusive. Small wood cells and well-developed annual rings may indicate seasonal variations in temperature also. Coal formation was greatly reduced in the Permian swamps and, during upper Permian time, was nearly unknown except in a few parts of the world.

Coincident with, and probably in consequence of, seasonal diversity in the latest Pennsylvanian and Permian, which are periods of extensive red beds deposition in America, there took place a differential evolution of the gymnosperms, with the development of plants closely resembling, if not indistinguishable from, cycads, and of coniferous types closely allied and probably lineally ancestral to the modern Araucaria and the Gingko. The Araucariæ are now reduced to a few species, while Gingko is perhaps technically extinct, it having been preserved by cultivation under religious auspices. This was the period of development of the gymnospermous seed with capacity for surviving one or more seasons unfavorable for germination.

Notwithstanding the evidence for seasonal changes, the writer has not been able to recognize in the Permo-carboniferous swamp floras, either of the United States or in western Europe, proof of severe freezing or seasons of actual winter of such severity as is characteristic of the region embracing Baltimore, Cincinnati, and St. Louis at the present day, although early Permian time witnessed extensive glaciation, even in the tropics, in India and at low altitudes in temperate regions of Australia, south Africa, and Brazil.[11]

[11] D. White: *Jnl. Geol.* (1907) **15**, 615.

Climate of Mesozoic and Tertiary Coal Fields

Inspection of the fossil floras of the Cretaceous and Tertiary coal swamps points, in every case, to ample or moderate rainfall and relative mildness of climate. Some of the Cretaceous coals, even including those laid down in central Alaska, were deposited in environments probably no colder than that of Wilmington or Charleston on the Atlantic Coast. In other cases, the climate may have been subtropical. Nowhere do we find evidence of semi-aridity or of very severe cold, though frost, possibly somewhat severe, doubtless prevailed in the winters of some of the Tertiary coal fields surrounding the Arctic and occurring even on the Antarctic Continent. A noteworthy feature of these circumpolar coal fields of all ages is the existence of old soils, as in other fields, the woody composition of much of the coal deposit itself, and the apparent absence from the coal-forming areas of Arctic climate as it exists today. Trees of large size were abundant in the coal-forming swamps nearly up to 82° north latitude and at about 80° toward the South Pole.

The distribution of coals in the high latitudes in the Mississippian, Jurassic, Cretaceous, Eocene, and Miocene formations, and the evidence presented by the coal plants for comparative moderation of climate in the regions of coal formation, strengthens the writer's belief that in the determination of climate and changes of climate, the epicontinental seas (their distribution, depth, form, size, etc.) were little inferior in importance to the continental configuration or the intercontinental connections. In comparing the climatic environments of both our older and our younger coal fields with present climates of the same regions, it should be borne in mind that the continents now stand high, perhaps near the maximum; many of the mountain ranges are young and still growing; the ocean is driven far down the continental shelves, and the epicontinental seas are drained or greatly reduced. From the geological viewpoint, present world climate is abnormal in its distribution and abnormal in its extremes. The earth's crust may be regarded as still in the midst of the post-Tertiary diastrophic revolution. The fluctuations in tide level and the deformation of the land probably were not greater or more frequent during the deposition of the Paleozoic or Mesozoic coals and their environing strata than they have been during the insignificantly short interval of Pleistocene time.

Deposition of the Coals

It has been pointed out that, in general, coals of the ordinary or common (woody) types were laid down in swamps in the form of peat. The typically woody coal was laid down in forested swamps in which a thin covering of water lay over most of the ground between the trees during at least portions of the year, the conditions being most like the swamps near the coast of the South Atlantic States before draining, and in some

of the tropical peat-forming swamps, such as those in some of the East Indies. Variation in conditions is plainly seen to have prevailed much as in peat-forming regions of the present time, though in the areas and times of widespread coal deposition the topographic relief was much less than at the present day.

In the paper by Doctor Thiessen, it will be shown that our coals present most, at least, of the features of composition seen in recent peats, though none of the extensive deposits of commercial purity were probably laid down in regions of so severe climate as peat of the Arctic tundra.

Water Level and Stagnation

Variations in the structure and character of the layers of the coal bed from point to point in the vertical section are mainly due both to the water level and to the composition of the water.[12]

Where the water covered the surface of the organic deposit and was at the same time so stagnant as to conserve the so-called "humic" or "ulmic" or "ulmo-humic" products resulting from the biochemical decomposition of more or less of the infalling vegetation, the decomposition solution soon became so concentrated at the level of peat growth as to be toxic and destructive to the agencies, mainly bacteria, causing the decomposition of the vegetable debris, so that further decomposition ceased in the toxic zone. The latter may have reached practically to the surface of the water, or it may have extended but little above the level of the peat. While this toxic condition of the water continued, a large part of the organic debris that sank in the water became buried in the peat formation with but partial or very little decay. It is evident that if, under favorable climatic conditions, the growth of the vegetation were lush and the contribution of the vegetable debris were consequently voluminous, the growth of the peat deposit would be very rapid. Further, as the greater part of the vegetal contribution was composed of vascular land plants, including of course trees, the deposit was, accordingly, woody and overwhelmingly composed of carbohydrate material.

A slower rate of contribution of the raw ingredient debris tended to favor the aeration (oxidation) of the water and consequent further progress of biochemical decomposition. Lesser degrees of toxicity of the water, caused, for example, by dilution of the decomposition solution by access of more water, permitted the same result. When, on the other hand, the water was replaced by influx on the one side and drainage on the other, or if the swamps were torrentially flushed, the ulmo-humic toxic decomposition products in solution were more or less removed with the water, to which they gave the characteristic tea color; the toxicity was correspondingly reduced, and decomposition progressed much further

[12] This subject is more fully discussed in The Carbonaceous Sediments: Treatise on Sedimentation.

before it was finally checked at, or not far beneath, the surface of the peat. Beneath the latter, and at no great depth, lack of circulation permitted stagnation of the water in the peat, which consequently became fully toxic and preventive of further decay at a depth depending, naturally, on conditions.

Biochemical Decomposition Selective

It is important to note at this point that biochemical decomposition is selective. The different component parts and organic compounds found in the vegetable matter contributed to the formation of the peat (coal) vary in the degrees of their resistance to biochemical (bacterial) decomposition in an aqueous medium, as is more fully explained in Doctor Thiessen's paper. Therefore the actual composition, as well as the structure of the layers of the peat bed, depends more or less largely on the degree of toxicity at the surface of deposition. The soft and delicate tissues of the plant (*i. e.*, the parenchyma, the mesophyll, etc.) together with the protoplasm quickly disappear at the outset, unless the water cover is completely toxic to the microbes producing their decomposition.[13] If unchecked, decomposition extends to successively more resistant parts and organs, including later most of the woody tissues, and finally disintegrates everything but the outer, waxy, resinous, or waxy-resinous coverings of spores or pollen grains; some of the cutinized and more or less waxy or resinous cuticular formations; the most horny, waxy, fatty, or resinous coverings of seeds and fruits; the waxes secreted on the surfaces of leaves and stems, or in internal vessels and canals; the most resistant fatty or fatty-waxy deposits thickening the cell walls, stored in cell cavities, or deposited in the cuticles of some of the plants; and the resins of many kinds produced in the wood cells, in wounds, and on the surface of trees, leaves, seeds and fruits of many types. These plant products are almost entirely resistant to biochemical decomposition under water.

Effects of Changes of the Water Level

Essentially normal proportions of the resistant products are, naturally, laid down with the vascular, or woody, plant matter of the vegetation to which they belong in a deposit where biochemical decay has made little progress, though in these deposits the carbohydrate, or woody, matter vastly predominates. It is evident, however, that as the woody and other partly resistant compounds of the plants and trees successively yield to bacterial action, contributing their decomposition products to the aqueous solution which may thereby be made increasingly toxic, little except the most resistant plant products—exines, waxes, resins, etc.—is left to accumulate, they being, in effect, concentrated. Exactly this

[13] D. White: The Carbonaceous Sediments.

happens at times of replacement of the water, or oxidation by aeration of the water, or of exposure with leaching of the surface of the peat so as to permit the decomposition of the less resistant plant products and substances.

Woody or Xyloid Coals

Accordingly, we find some layers of the coal deposited in toxic water and composed mostly of logs, stems, twigs, ferns, etc., with spores and other resistant elements mingled in a natural proportion. Most coal beds contain such layers, which are conspicuously woody, or xyloid. In other layers, the amount of well-preserved wood may be less and less, the resistant debris being in larger proportions; in still others, very little woody matter remains and the deposit may consist mostly, if not wholly, of exines, fragments of cuticle, resin grains, scales or lumps, waxy secretions, and, rarely, particles of gum.

All these phases may be, and usually are, found—repeatedly—in a single coal bed. Layers or benches composed mainly of wood, twigs, etc. are somewhat irregularly intercalated with layers in which the wood is less in evidence and fine debris containing, of course, larger portions of resistant exines, etc. forms a larger part of the deposit. In fact, as might be expected, and as may readily be seen, there is complete intergradation from the conspicuously xyloid type to what may be termed the spore type.

Those horizons in which more or less of the wood, as well as the less resistant plant material, disappeared by decomposition are usually duller in aspect than the woody deposits laid down beneath a continuing and fully toxic water cover; and when, as so frequently happens, films or thin layers of mineral charcoal are present, the edges or transverse fracture surfaces of the coals are distinctly mat. To coal of such general physical constitution and aspect, a number of British investigators have applied the name "durain," evidently with the thought that it represents a distinctive chemical or physical ingredient of coals.[14] In effect, however, the term appears useless except possibly in substitution for such adjectives as mat, which is not readily understood by the miner, or dull, a term not so agreeable to the coal operator.

The occurrence of lenses or strips of bright coal bedded in the mat portions is common and familiar to all who handle coals. These almost invariably represent more or less flattened twigs, branches, and logs that did not succumb to the decomposing microbes before they were surrounded by a solution so toxic as to preserve them. Meanwhile, in the course of time, they became permeated by the ulmo-humic decomposition products and, as now dehydrated, compressed, and lithified, they present the aspect of vulcanized rubber in the lower rank coals; of jet in

[14] M. C. Stopes: On the Four Visible Ingredients in Banded Bituminous Coal. *Proc.* Roy. Soc. (1919) **90**, 470. M. C. Stopes and R. V. Wheeler: Monograph on the Constitution of Coal, 1918.

coals of bituminous ranks; and of obsidian in anthracites. They are readily distinguishable in lignites, as well as in anthracites, if the examination is sufficiently close.

It is not improbable that occasionally logs and branches were either driven down or sank of their own weight far enough into the organic ooze to cause their preservation for the most part, while at the surface of the peat the toxicity was not sufficient to preserve most of the wood contributed to peat formation. Toxicity for short intervals would permit the survival of wood in such strips or "stripes." To layers or benches of coal of the more or less woody type containing this densely humified woody tissue enveloped as lenses and strips in the mat (durain) layers, the same English investigators have applied the term "clarain," which wholly without reason according to the writer's judgment, has been put forward, like "durain," as one of "the ingredients of coal." It may be added that "vitrain," a term applied to another of the supposed "four ingredients" in the belief that it represents an amorphus or structureless accumulation of humic acid, comparable to dopplerite, appears to be only very densely humified wood or other plant tissue, in which, due either to too advanced carbonization of the coal or failure of technique, the vegetable structure was not seen.

Cannels

Where ponds, bayous, or very sluggish channels, too deep for the growth of trees, occur in the swamp, the agitation or replacement of the water favors more oxidation or flushing of the toxic decomposition products and permits the advanced decay of the reduced infall of land-derived vegetable matter, with the effect that little except spores and some resins[15] and waxes, left by the decomposition of the drifted land plant material, sometimes with occasional cuticles, remains in the organic ooze which at depth becomes toxic. Here the contribution of the organic matter is more or less uniform in substance though subject to some seasonal variation in rate, and the water cover is rarely, or only after a long time, reduced by filling of the depression or channel, so that we have a massive deposit, sometimes with very little evidence of lamination. This deposit is the typical *cannel*. It is always laid down in quiet water of slight lateral extent and too deep for land plants to grow in. If the mineral matter in the sediment is relatively large in amount, it becomes a "bastard cannel" or "canneloid," or it may verge into a cannel shale if larger amounts of terrigenous inorganic matter are included. Seasonal or unusual variation in the water level appears to result in lamination which, however, may not show until the deposit is buried, lithified, and weathered.

[15] D. White: U. S. Geol. Surv., *Prof. Paper* 85 (1914) 65.

Fat Cannels

Not infrequently minute floating algæ—"water flowers," such as *Reinschia, Pila, Glœocapsamorpha,* or *Elaeophyton*—live in the pond or bayou and the undecomposed or but partly decayed remains of some of the more fatty or resistant of these mingled with the exines and other normal constituents of the cannel, which the algæ[16] enriched by their generally waxy composition, the latter being high in hydrogen and comparatively low in oxygen.

Algal Coals

Where, as in larger bodies of stagnant or nearly stagnant water, which may be alkaline, the fatty algæ formed the greater part or even the entire deposit, we have the typical boghead, with its characteristic capacity to yield large amounts of artificial petroleum by destructive distillation.

Lamination of the Coal

Lamination characterizes practically all coals and is seen on close examination in anthracites and sedimentary graphite. Seasonal or irregular flushing may cause lamination. Ordinary obscure and exceedingly thin lamination, not attended by deposition of "mother of coal" is, however, probably correctly to be explained by seasonal variation in rate of contribution of the vegetable debris, by variation in the depth and concentration of the water, and by seasonal changes of temperature, all of which are found to produce lamination in recent silty deposits. It is, in fact, hardly to be doubted that the minute lamination has all the refinement of annual change in deposition. Brief seasonal exposure is not improbable, especially when the laminæ are strongly marked as well as exceedingly thin.

Muck Films

Most coals show, however, a grosser and more variable lamination presenting phases which are hardly to be explained, except by exposure or oxidation of the peat-forming surface. That such exposure occurred from time to time is plainly shown by the thin layers or films of mucky soft matter resulting from the oxidation of the top of the exposed peat, which, in fact, was being transformed to muck. Such layers are seen even in anthracite. They probably indicate exposure for more than a very brief season.

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[16] See B. Renault: Les Micro-organismes des combustibles fossiles, 1893; H. Potonie: Entstehung der Steinkohle und der Kaustobiolithe, 6th ed., 1920; M. Zalessky: *Bull.* Soc. Geol. Fr. (4) (1917) 373; D. White, and T. Stadnichenko: *Econ. Geol.* (1923) **18,** No. 3; R. Thiessen, U. S. Geol. Surv. *Prof. Paper* 132-I (1924).

Fusain (Mineral Charcoal)

Other conclusive evidence of exposure, at times, of the surface of the peat is seen in the occurrence of fusain (mineral charcoal or mother of coal) strewn or matted in layers on the bedding planes of the deposit.

The prevalent belief that fusain is the result of forest fires, either *in situ* in the immense swamps, or on adjacent higher ground from which the charcoal was washed out over the swamps is quite incompatible both with theory and fact. The assumption that it results from fires on the surface of the exposed peat is inconsistent with the great extent of the fusain layers, the evenness of the bedding, the absence of corrasion pits or ash accumulations with supposed cinders, the normal state of the coal just beneath the fusain, the regularity and parallelism of the distribution of the fusain, generally in thin layers, the sometimes almost incredible closeness of the layers which may form a large part of the deposit in some of the beds, the purity of some of the layers, and the delicacy and orientation of some of the carbonized debris. Fortuitous forest fires could hardly have been so frequent and so regularly recurrent over the same great areas, and so widely destructive as these should have been, without leaving traces of ash accumulation or residue.

That the fusain cannot be charcoal drifted out from the land is shown by the continuity of its deposition; by the arrangement in normal position or relations of the "charred" fragments of such delicate material as fern fronds, pinnules and stipes, not to mention stems and branches; by the inadequacy of any transportation current to distribute charcoal evenly again and again throughout the great areas in the midst of the growing vegetation, and, especially, to do so without an accompanying film or sheet of land-derived mineral sediment, and, finally, by the inadequacy of any probable supply at the source. To assume that the erosion which would transport these vast quantities of charcoal out over thousands of square miles of coal-forming swamps would not at the same time erode the soil as well as wash away the plant debris is inadmissible. On the other hand, the fossilized peat surface offers no sign of erosion, nor of submergence beneath waters not the most tranquil.

In another publication discussing the origin of fusain,[17] I am pointing out the insolubility of the "ulmo-humic" decomposition products in water at ordinary temperature after they have once been concentrated and dried, as pointed out by Collin Rae[18] and others. With this fact in mind, the fragments of wood, bark, stem, fern leaf, and other debris, now fusain, covering innumerable bedding planes in the coal may be regarded as undecayed or partly decayed plant debris lying on the surface at times of exposure of the peat by evaporation of the water cover. Under these conditions, the evaporation-concentrated toxic decomposition matter

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[17] The Carbonaceous Sediments.

[18] Collin Rae: Amer. Assn. Pet. Geol. *Bull.* (1922) 6, 334.

in the solution, impregnating and drying on the surface of pinnule, stem, and wood fragment would not only protect them for a time under weathering, but by the insolubility and toxic composition of the film or crust coating the fragments, would leave them protected and resistant to the renewal of microbian action, that is, further decomposition, on resubmergence, and the resumption of peat deposition.

In some coal beds and in benches of other beds, presumably laid down in a persistent water cover of the swamp, layers of fusain are relatively rare or even wanting; in others, they appear to form a large part of the coal. Rarely, it forms thin beds or lenses several centimeters in thickness. In some cases, it is jumbled and confused as by slight wave action. It is common in anthracite, though it appears to have been crushed in the course of the great pressure stresses to which the anthracite beds have been subjected. To a considerable extent, the thicker layers in anthracite are rubbed and eroded in the process of preparation of the coal for the market. Pennsylvania, Colorado, and Washington anthracites are apt to break along bedding planes covered by fusain, in spite of an apparent partial cementation in these layers.

Fusain is probably the source of the greater part of the dust in mines, tipples, and crushers of anthracite and other coals. Its structure, porosity, and friability suggest it as the principal source of the exceedingly comminuted and most easily ignited mine dust.

Effects of Water Conditions on the Initial Composition of the Deposits

As foreshadowed in the discussion of the conditions of deposition of the xyloid and the spore coals, and of the formation of cannels and bogheads, a very close relationship exists between water conditions and the initial chemical composition of the coals; *i. e.*, in the peat stage. In the typical woody deposits, for which a thin perennial stagnant and toxic water cover is most favorable, the carbohydrates (lignocellulose, cellulose, etc.) form the greater part of the solid organic matter and as the coal passes through its subsequent alterative changes, its chemical composition is dominated by products of carbohydrate derivation.

On the other hand, where the water conditions favor the decomposition of the less-resistant organic debris and where even the greater part of the woody (carbohydrate) material decays, a large portion, perhaps nearly all, of the carbohydrates goes into the colloidal decomposition solution, more or less of which is carried away in the drainage of the swamp. The portion remaining in solution has lost its carbohydrate character through biochemical transformation, as will be shown in other papers of this series. Accordingly, in these deposits the chemical effects of the non-carbohydrate elements in the spores, resins, waxes, and other fatty plant secretions and products are more and more marked, they

having been brought into prominence by the disappearance of an otherwise overwhelming amount of woody matter. It is to be noted at this point that the resins and waxes, and the other resinous, woody, and fatty plant products, such as the spore and pollen exines, and the fragments of cuticle, which are resistant to decay under water, are characteristically high in hydrogen and low in oxygen, quite the reverse of the carbohydrates. Therefore, as these form larger proportions of the organic sediment, the deposit becomes "richer," *i. e.*, it is relatively higher in hydrogen and lower in oxygen and, in general, much higher in volatile matter. This is well illustrated by the cannels in which the woody tissues are reduced nearly to obliteration, though they doubtless contributed much to the decomposition solution now hardened as binder or groundmass in the deposit.

Still greater richness in hydrogen and volatile matter is added when, as in many of the cannels, fatty algæ, especially microscopic colonies of one-celled algæ of certain kinds with thick, waxy, or fatty cell walls mingle with the other plant debris of the deposit. Consistently, the bogheads, which are made up largely or almost exclusively of such algæ, are the fattest (the most richly hydrogenous, and the most productive of volatile combustible matter) of the entire series of carbonaceous organic sediments. Not only are these bogheads, or algal coals, productive of oil in greatest amounts, sometimes as much as 135 gal. to the ton, when distilled, but the distillates produced by methods approximating as far as possible natural geological conditions approach nearest to the natural petroleums.

Variation in the amount of volatile matter in different layers of a coal bed is largely due to variations in the proportions, or in the concentration, of spore and other "fatty" ingredients, as compared to the amounts of woody matter, especially fusain, in the deposits.

The chemical contrasts between the types of coal, due to differences in the chemical composition of the ingredient debris and decomposition products, are greatest in the initial or early stages of alteration of the peat to coals of higher rank. Eventually, as will be pointed out in another paper, these initial chemical differences are obliterated as the deposit approaches the rank of anthracite. Meanwhile other distinctions develop as the result of geochemical changes in the buried deposits under geodynamic influences.

DISCUSSION

Edward C. Jeffrey,* Cambridge, Mass.—The statement that the natural layers of coal represent a high degree of biochemical change is one to which I cannot subscribe because the microstructure of coal shows

* Professor of Botany, Harvard University.

that the matrix layers are unusually well preserved. The matrix layers show a great deal of structure, more than the shining layers of coal.

As regards the origin of mother of coal, I also disagree with the author. I have microscopically examined a great deal of coal from all parts of the world and I think he has changed his attitude regarding mother of coal. Some years ago he thought that it was due to the action of the dry-rot fungus, or some similar organism on wood. If that were the case, the fungus would show some evidence of its presence, either the actual body of the fungus would be present, or, if, the body disappeared, the holes that it always makes in the cells would be seen. Neither of those phenomena can be observed to any extent in mother of coal; I have examined an immense quantity of it. From the comparisons of recent deposits in water with coal, I have come to the conclusion that mother of coal is exactly what it is often called, mineral charcoal, the result of former forest fires. I think that is the only hypothesis that fits all the facts.

George H. Ashley,* Harrisburg, Pa.—One phase of this subject has not been touched on, though it is one on which we have all thought a good deal and which has more or less bearing on the general physiographic conditions in which coal is laid down; that is the origin of the thin partings. The more I have studied these, the more the question has arisen, in my mind, as to whether wind action may not have to be drawn on to account for the laying down of such very thin layers of practically uniform thickness, in many cases over hundreds or thousands of square miles. These thin partings seem to be of a different character from partings, here and there, that thicken toward what might have been a shore, as though they had been washed in by water and feathered out. These thin partings are often ¼ in. thick and, as in the Pittsburgh bed or in the beds of the central interior field, sometimes can be traced over very large areas. What is known as the blue band in the No. 6 coal of Illinois, covers several thousand square miles and has a thickness of about 1 in., yet I cannot see how such a uniform bed could be laid down by water currents. It is a difficult thing to picture those conditions adjoining these great swampy areas.

Reinhardt Thiessen,† Pittsburgh, Pa.—I am glad to have my theory of the origin of the thin bands of shale in coals expressed; I believe they are wind-born deposits of eruptions probably, though many crystallographers disagree with me.

During the last three years, in my work on the correlation of coal beds, I have observed that all the coal beds in Ohio, West Virginia, and western Pennsylvania have been laid down in subsiding areas. The coal

* State Geologist of Pennsylvania.

† Research Chemist, Bureau of Mines.

always begins at the bottom, with what I call anthraxylous coal, and in going toward the top of the bed it becomes more and more attritious. I think that at first it was a typical woody swamp and the moisture conditions increased until we had a typical aqueous swamp—the woody plants gradually giving way to more and more swamp-loving or water-loving plants until the whole area was covered by a typical aqueous swamp and finally by shallow water. At times, the subsidence seems to have been retarded and woody plants again appeared, but the surface seems to have subsided again and aqueous conditions continued until the area was covered by silt; very often the coal ends with a cannel coal, as is typically shown in the Freeport bed, showing that the aqueous stage was prolonged.

S. W. Parr,* Urbana, Ill.—If we were to accept the fire theory of the origin of mineral charcoal, we would have to diagnose a kind of fire that has left a very uniform type of material. We calculated to the pure organic material, according to a habit of calculation that we have developed in our laboratory, that it would have stopped at a volatile constituent in the pure material varying only 2 or 3 per cent. That would seem to be very difficult from the fire standpoint. From 17 to 19 per cent. of volatile matter is uniform with regard to this type of deposit. If we may accept a dual form of mother of coal, in which there is a higher ash content and in which the volatile factor is a little bit higher in one than in the other, we find another peculiarity of this substance. The normal mother of coal has no ash other than what we expect to be present in the wood ash and very low, corresponding in terms of the ash factor for the glance coal.

The other type of mineral charcoal, quite as unfortunate as fusain from my standpoint, sometimes runs as high as 25 per cent. in ash. All these high-ash layers are characterized by a very high sulfide of iron or very high carbonate of lime. That suggests that the very porous layer of mother of coal has had a secondary infield tracer and we frequently find calcium carbonate and pyrites associated. The heat value of the organic material in any of these types is almost exactly the same as pure organic substances of the coal.

David B. Reger,† Morgantown, W. Va.—The partings in coal interest us all very much and puzzle us even more; still I am loath to believe that any theory can be successfully established that calls for the transportation of this foreign material in solid form from a distance into the coal swamp, as it would be most irregular and unnatural for the same thickness to be carried for thousands of miles. If this were volcanic

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† Assistant Geologist, West Virginia Geological Survey.

matter, as has sometimes been claimed, it would necessarily be thicker at the source than farther out in the swamp, and the same thing is true of silt. But suppose that muddy water formed it. Every coal swamp has a small amount of silt in solution; then as the water evaporates (either slowly or rapidly as you please), having had a more or less constant depth over the swamp, there will be a deposit of probably uniform material with fairly uniform thickness, because a certain percentage is all the time coming out of the evaporated water as long as the water is in the swamp. Possibly, in the process, the water is agitated gently and the material is kept partly in solution, so that it settles slowly down into the peat and becomes a part of the coal and does not become a noticeable layer but is disseminated through the coal in formation. Of course, this process does not make a noticeable band, but if you assume that the water was evaporated quickly during some cycle of uplift or draft, it is easy to suppose that there will be a silt layer of constant thickness and perhaps fairly constant extent, just as we find the partings in the coal beds.

Wilbur A. Nelson,* Nashville, Tenn.—During the past year, some of the clays in the coal measures in Alabama have been found to be made up of volcanic material. Samples of those clays have been sent to the United States Geological Survey and they show Bentonitic material, as we have been calling it. The thickness of partings in coal seams could readily be accounted for as coming from a volcano, if the volcano was very far away. It is only when very close to the volcano, that there are great differences in the thickness of the ejected material. In the Mississippian rocks, there are many layers of clay that are very full of volcanic material—Green Bentonitic clays. This recent discovery in the coal measures in Alabama would indicate that if we study the coal measures more carefully, we will find other clays of a volcanic ash origin in these measures.

Reinhardt Thiessen.—The evaporation theory is not good in this case because plants, as we find them in the coal measure, will not grow in deep or even shallow water. I paid particular attention to the Freeport bed, where the coal comes up normally, that is, woody coal gradually becomes more and more mixed with mineral matter. In other words, the mineral matter in the bone begins in the first inch with the normal mineral matter content of the coal and increases gradually up to about 20 per cent., and from there on it stays rather constant or increases slowly until it reaches the maximum; then it gradually disappears until the coal again assumes the normal character. If we should imagine the peat covered with water to such a depth that we should have precipitation of, say, 11 or 12 in. of mineral matter, such a submergence would have killed off all the swamp plants living in it.

* State Geologist of Tennessee.

George H. Ashley.—The idea of volcanic origin of these thin beds appeals to me; they have been scattered through the whole body of our coal measures. What we call the "flint-clay bed" runs from central West Virginia into northern Tennessee; it is well down in the Pottsville. The Pittsburgh bed is near the top of the "Coal Measures." To account for these thin partings by assuming volcanic eruptions every time a coal bed was being laid down is stretching our credulity. The only other solution is to say that whirlwinds sweeping over practically desert areas lifted this matter very high in the air and allowed it to drift over and settle on these large swamp areas. I know of no conditions where similar deposits are being laid down in areas adjoining our deserts. It is difficult to think of large deserts adjoining swamp areas, but this solution may have some bearing on our ideas of the origin of the coal.

Wilbur A. Nelson.—I will not say that all partings are necessarily derived from volcanic material, but I believe that many will be found to have that derivation. In a study of the coal fields of Tennessee, we have found a series of three or four parallel troughs. As one filled in with sandstones, shales, and coal beds, it was filled out to a barrier reef a distance of 10 to 15 miles; and then comes the next one, and then the next. That does not seem to agree with the theory of deserts next to the coal deposits. A very detailed study has shown this to be the condition of deposition in the southern half of the Tennessee coal field, and it is the same condition that has been thoroughly established as being responsible for the deposition of the Paleozoic formations in the great valley of east Tennessee.

Edward C. Jeffrey.—The question of the partings in coal, so far as they are produced by the substance known as mother of coal, should be envisaged and looked at from the standpoint of actual deposit. No doubt there are continuous layers of the charcoal from burnings on the land in actual peat deposits laid down in water and, further, not only are there continuous layers, but also isolated pieces of charcoal more or less irregularly diffused throughout those deposits. The only rational theory is that this charcoal originated from land fires and was washed into the water where it floated and sooner or later sank. For example, after a fire, I noticed quantities of charcoal floating on the surface of Lake Huron, and I imagine that is not an uncommon occurrence.

James F. Kemp,* New York, N. Y.—We should be careful to discriminate between what is native and what is infiltrated afterwards; the mention of carbonate of lime and pyrites would suggest that a large part of this material was infiltrated. I hesitate to speak closely about the actual composition of mineral charcoal, but the subject has interested me

* Professor of Geology, Columbia University.

because fossil Calamites are commonly visible in it. I presume that there were high-silica plants in Carboniferous times, very much as there are today, and that these might have formed a framework contributing a very high ash, compared with other forms of vegetation. The fumes of calcite and gypsum and other evidences on the joints in the coal show that there has been a good deal of infiltration, which would naturally go into the most porous parts of the coal, and those parts are the layers of mineral charcoal.

E. S. Moore,* Toronto, Ont.—It would be difficult to assume that these thin partings in coal seams were formed by evaporation. When you examine the composition of such a deposit, you would expect it to be very much higher than it is in the substances, like calcium carbonate, usually carried in solution, relative to the other constituents. It is also difficult to assume that the partings all represent volcanic deposits. The only logical explanation that I have been able to find for them is in supposing that in times of high water some streams laden with fine sediment have broken levees and flowed over the swamps, spreading the sediment over very large areas.

I have just read Doctor Jeffrey's work on Coal and Civilization, in which he so strongly urges the charred-wood theory for the origin of this material and have wondered whether he has not made the same error that so many of our mineralographers make in explaining our problems in ore deposits in the laboratory without reference to the structures in the fields. For a number of years, I have observed all the swamps associated with the burned areas I have come across in northern Canada and elsewhere, but I cannot see the possibility of obtaining the relative proportions and the associations found between the mineral charcoal and the other coal by any means of having this material washed in from burned areas in a region where you are going to get the great coal seams laid down. When most of the charcoal is carried off the burned lands into the bodies of water, great quantities of mineral sediment are carried in at the same time.

Edward C. Jeffrey.—Lands covered by vegetation, except under very unusual conditions, where there is a great fall of water, do not undergo erosion. My attention was directed to that a number of years ago, when studying plants growing in wet places, and I looked in vain for the seedlings until it occurred to me that they might make their appearance where the soil had broken away, and by searching there found them. It is easy to exaggerate the question of erosion in low areas, such as it is generally agreed, in the theory, that coal deposits were laid down. I do not believe that mineral sediments were laid during the active coal-formation period. At any rate a very large volume of it was water with mineral absorption solution.

* Professor of Economic Geology, Toronto University.

Doctor Kemp is entirely right in his view that the mineralization of certain mother of coal, so-called, is due to the mineral substances in solution in water. It is not usually the case that lignite debris deposited in the clay beds are filled with pyrites. Wood is the natural resting place of mineral matter, and we are investigating now the formation of crystals in plants. It has been supposed that it was the laying down of crystals that made the mother of coal; that is, a coal or a matrix was laid down first and the crystal was laid down in that matrix. It is apparently a parallel case.

George H. Ashley.—In the block-coal field of Indiana, there are three or four beds that consist of alternating layers of bright and dull coal. These beds run as much as 5 ft. thick, while the dull and bright bands run not less than twelve layers to the inch. The whole bed is composed of alternate layers of mother of coal and glance coal, so that any explanation of mother of coal must provide for such a repetition of conditions as will produce these thin bands. The coal of those beds is characterized by being in small pockets, or basins—as many as four pockets have been mined in one small mine while some basins may be 15 or 20 acres in extent; the coal is limited to the basin, except possibly the topmost layer, which may run from one basin to another. That layer is not of the block character; it does not have mother of coal, but is "bituminous." There seems to be, therefore, some relation between the small basins and the presence of the mother of coal. These small basins cover a large part of the eastern side of the Indiana field; so that a thousand square miles may be covered with these small basins of coal. The most reasonable explanation seems to be that these small basins have dried up during each dry season, or during especially dry seasons and the layers of mineral charcoal represent the dried surface of the peat.

Edward C. Jeffrey.—The mother of coal is not uncommon in cannels and oil shales, formed continuously under water cover.

Homer G. Turner,* Bethlehem, Pa.—My observations on anthracite have shown that, aside from any possible mineralization by means of pyrite or other minerals, there are several kinds of mother of coal. They vary from materials which are difficult to scratch with the thumb nail, to those which are easily pulverized between the fingers. The hard materials show under the microscope either crushed cells or perfect cells with thick walls. The soft materials show perfect cells of the same type as those of the hard except that the cell walls are thinner. There seems to be every gradation from anthraxylon to material that closely resembles ordinary charcoal. This gradation suggests that chemical

* Assistant Professor of Geology, Lehigh University.

reaction is a more logical theory for the origin of mineral charcoal than is the theory of forest fires.

David White.—We all agree that mineral charcoal (fusain) is present in coals of all ages since the beginning of forest growth on land. All the common types of post-Devonian coals contain it; in some coals it is very scarce and in some incredibly abundant. Sometimes the layers will not be ½ mm. thick in matter seemingly evenly spread; yet, when examined closely, it will be found that neither the fusain nor the enveloping matter is distributed evenly.

"Mineral charcoal" consists of fragments of plant tissue not fully decayed. It embraces all kinds of wood, according to the geological period. In many of the Carboniferous beds there is no readily visible trace of Calamariæ; equisetums and horsetails were relatively scarce in the Tertiary swamps. Sometimes we find the most delicate fusain material scattered in these infinitesimally thin layers, hardly separated one from another by an appreciable thickness of glance coal, ordinarily not over ½ mm., and rarely more than 1 cm. in thickness. Very delicate pinnules of ferns in which the nerves are transformed to fusain are sometimes found in the "mineral charcoal;" these must have been transformed in place in the swamp.

We sometimes make the mistake of predicating conclusions as to coal and its formation on an intensive study of a single bed with which we are particularly familiar or which we have subjected to special examination. I am perhaps quite alone in my theory of mineral charcoal (fusain). The assumption that this material has drifted in such enormous quantities as to make up the greater part of the coal beds in some of the swamps is utterly incompatible with any assumption that coal is laid down in an immense swamp; the vegetation necessary to produce the coal could not grow in a swamp of such vast extent if the circulation was so unobstructed by vegetation that charcoal drifting from upland or border land perhaps 60 to 70 miles distant has come unobstructed, and has been scattered in a thin layer over thousands of square miles. The extraordinary continuity of the fusain layers and their close proximity to one another, often with less than one-half millimeter of intervening ulmic matter, makes the drift theory little short of preposterous. On the other hand, the total amount of charcoal in some of the coal beds is really enormous. It can not have come from the land.

It is hard to understand how the charcoal would be formed in such great amounts on the land without destructive fires that would do more than destroy the growing tree—would probably denude the land. If there were a run-off such as is necessary to gather the charcoal and carry it out over the great swamps, this run-off could not possibly have failed to have extensively eroded the undersoil, stripped by the fires and laid

bare for erosion. We would have had enormous amounts of ash in beds in which the charcoal brought by transportation was accumulated in such great amounts.

If the mineral charcoal were actually charcoal remaining from forest fires, coal beds containing large quantities of it should be relatively high in fixed carbon. On the other hand, the slight variation in the fixed carbon of layers containing much mineral charcoal accords with my explanation of its origin. The humic matter of the deposit not only enveloped carbohydrate material but partly transformed and, to an extent at least, it impregnated the woody debris.

From the circumstances of deposition of coal, it must happen during the long period required for the sedimentation of a thick bed that, due to the varying rate of subsidence or filling of the basin, the peat will at times be built above water level, so far as this may have been practicable, with occasional development of muck layers as the result of oxidation of the exposed peat; or, on the other hand, the vegetation will have been drowned out as a result of too rapid submergence. In the latter case, freer circulation of water over the submerged swamp would facilitate the distribution of fine silts and mud in muddy water, which would gradually settle in a layer possibly very thin but extending with relatively uniform thickness over great areas. Similarly, breaching of barrier bars as a result of too rapid subsidence would permit incursions of the sea, possibly with inwashing of sand over the peat. If the sea remained, even a short time, the fresh-water vegetation from which normal peat is formed would be killed, and if the excess of marine water was adequate marine fossils may have spread out over the swamp. Lingula and Discina were best able to endure the acid peaty bottom conditions. Goniatites apparently were relatively hardy. With clearer and less acid water conditions, marine mollusca, including coral, may have invaded the swamp. Of course, if the sea was not shut out and the surface of sedimentation was not raised sufficiently by deposition of marine organic and inorganic matter, peat formation will have terminated and we shall have a marine shale or argillaceous roof over the peat previously formed. On the other hand, if the sea was excluded and the water cover was sufficiently reduced in thickness, fresh-water peat-forming vegetation of the normal types will eventually recover the old area. Marine partings, with marine organisms, may be not more than an inch in thickness.

Limestones partings are extremely rare but, in the coastal swamp peats (coals), marine partings are probably more frequent than is generally supposed.

Partings resulting from flooding from the landward side of the swamp are characteristically more or less distinctly wedge-shaped and should be thicker and more arenaceous in the direction of the source of the sediments.

I recall a number of volcanic explosions—Kilauea, Martinique and Katmai—that have contributed dust of rather widespread extent. A thin layer of volcanic ash settled on the pools and housetops at Newport, R. I., after the eruption near Martinique. The presence of volcanic ash in coal partings is not remarkable and, in view of the considerable time that may have been required for the deposition of the "blue band," in Coal No. 6 in Illinois, is rather to be expected and even looked for. However, I cannot admit that much of the inorganic detritus, not volcanic or cosmic, that makes up the ordinary coal parting, was blown to its present geographic position by the wind. The degree of aridity predicated by such eolian transportation is incompatible with the luxuriance of plant growth which characterizes most of our coal deposits. Certainly, a combination of wind-blown inorganic sediments with charcoal of forest-fire origin prepares one to expect a percentage of ash in the charcoal partings that is not present.

A. C. Noé,* Chicago, Ill. (written discussion).—This paper gives the condensed substance of an entire textbook on coal geology. It contains all essential facts in the history of coal deposits and allows us to visualize the processes of nature by which the great coal swamps were produced, were covered up again, were changed, and lifted out of place. The mining engineer may well be stimulated, by this paper, to look upon the peculiarities of the coal seams from an evolutionary point of view and to understand them better.

W. A. I. M. van Waterschoot van der Gracht, Ponca City, Okla. (written discussion).—This paper is an excellent and singularly complete description of the nature of the Palaeozoic and Mesozoic peat swamps, and the various conditions and factors that influenced the deposition and character of our coal beds. Unfortunately, I am less familiar with the American coal deposits than with those of Europe, but the author's statements apply to conditions observed in the Coal Measures deposits of northwestern Europe, from Silesia to the English Midlands and Scotland. Here also we have a broad and flat coastal zone along a very shallow epicontinental sea, to the north of a slightly rising continent: the first warping of what would later become the Hercynian-Armorican front ranges. This epicontinental sea also had a northern shore, revealed only in the Coal Measures of Scotland, but buried farther east under the Mesozoic and Tertiary deposits of the north German plains and the Baltic.

Here, again, we find in the Lower Coal Measures singularly wide and uniform swamps, succeeding largely arenaceous and dominantly marine conditions. This densely overgrown, wide, flat coastal plain was entirely unbroken, except by occasional estuary lagoons and lakes. The same

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coal seams can be traced from eastern Westphalia all the way through Holland and northern Belgium, and very often it seems that some should be correlated to such in northwestern France and even in England. This correlation is doubtlessly possible for some of the major marine invasions.

There apparently was a tendency for slightly deeper water west of the Rhine, in Holland and in the Belgian Campine, where the barren facies of the lowest Coal Measures gradually extends higher up in the series, consisting of a preponderance of massive, finely sandy shales, filled with a hash of mostly much decomposed and undeterminable plant debris.

In the middle Coal Measures, conditions become more variable: the coal seams, though thick and numerous, succeed each other rapidly, and are of far less lateral extent, indicating more differentiated and changing swamps of lacustrine character in wide and very flat lowlands. Marine invasions are practically absent, indicating that marine conditions must have retreated to considerable distance.

In the upper Coal Measures of Westphalia, Holland, and Belgium, conditions become still more irregular and the coal seams are usually full of intercalations of finely sandy shale beds. At least temporarily, marine conditions also become more frequent again and indicate occasional deeper submersion, sometimes depositing a thin limestone. Farther to the north, however, the few outcrops, limited to a few uplifts in the Teutoburger Wald, mark the prevalence of a more barren red bed facies with very few coal seams.

The uppermost, Stephanien, series is not represented in the known northern area, having been eroded before the deposition of the middle Permian, which (after the main diastrophism) commenced as a new shallow epicontinental sea (the Zechstein), which soon changed to a widespread saline formation and red beds, which continued all through the Trias.

The marine invasions in the productive Coal Measure series but rarely deposited thin marls or limestones with brachiopods; they generally consist of an often extremely thin black shale bed with minute dwarfed or very young goniatites and a few lamellibranchs; lingula is generally present and very often is the only indication of salt or at least brackish water conditions.

In the middle Coal Measures, coarse sandstones are entirely absent, only fine-grained sandy shales or fine shaly sandstones are found as intercalations in pure mud shales; higher up in the series coarser or even conglomeratic beds appear again, indicating nearby higher ground and stronger precursory earth movements of the orogenic phase of the late Carboniferous-Permian diastrophism.

All that the author says of the deposition of the coals holds true for the European Coal Measures. His description is so good that, in reading it, we almost feel transferred into these boundless tepid swamps of the remote

past, with a vegetation so luxuriant that even the immense lush tropical swamps of Sumatra must fall far behind such riotous growth. In Europe, we observed that when water apparently became deeper, drowning out the vegetation in a swamp, Calamites apparently continued to grow longest in such lakes; while on the contrary, if lack of moisture seemed to have stopped peat deposition, the upper layers of the coal bed consist of dull mineral charcoal. When a salt-water invasion put an end to the growth, siliceous or calcareous "coal balls" are common. How far should the Glossopteris flora in Arctic and southern Gondwana Coal Measures be interpreted as an indication of a different, possibly colder climate?

David White (author's reply to discussion).—While it is more difficult to reveal the structure in the glassy layers of the coal than in the mat layers or "durain," where much refuse showing structure may be discerned with the naked eye, abundant debris of structural organization is present also in the former.

As to formation of mother of coal, Professor Jeffrey attacks a theory long abandoned by me. I hope, on the other hand, that I have shown that the old theory supported by him is untenable, whether or not my substitute explanation is later fully established.

I agree entirely with Doctor Thiessen as to the evidence of variations in the depth of the water cover, due to varying submergence, and their effects on the progress of biochemical decomposition and on the mechanical constitution of the sediments; but not as to the frequency and volume of partings composed of volcanic ash or dust carried by winds.

The Microscopical Constitution of Coal*

By Reinhardt Thiessen,† Pittsburgh, Pa.

(New York Meeting, February, 1925)

INGREDIENT MATERIALS OF COAL

In the general study of coal, all evidence points in the one direction—that coals had their origin in a manner analogous to that of peat. The best method of studying coal, whether it concerns its chemistry, composition, or physical condition, is to study peat. The essentials in a study of peat are a knowledge of the chemistry of plants, knowledge of decay and of the transformation process of plant-substances into peat. A number of facts must be emphasized, namely, (1) peat is formed under wet conditions only; (2) plants grow in the place where peat is formed; (3) all the plant substances go into the bog; and (4) all the plant substances are subjected to a series of phases of decay which are (*a*) in the air completely above the water level but in relatively moist conditions; (*b*) above the water level, but covered by debris; and (*c*) completely submerged by both water and debris.

Plant Chemistry

Plant chemistry as a whole is remarkably well understood. The number of compounds composing plants is large, and it is not possible here to give even a comprehensive outline, but a classification into definite groups is possible; this is as follows:

Carbohydrates; glucosides; pigments; tannins; acids, alcohols and ketones, etc., and their salts; essential oils; resins; vegetable bases; proteins; enzymes.

Plant substances may also be grouped according to the role they play in the life of the plant, such as:

Framework materials, living materials, food materials, protecting materials, waste materials.

While this classification groups them well for certain purposes, it does not group them exactly chemically; but in a consideration of the composition of coal, this is an excellent classification for our purpose here.

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Carbohydrates

This group is a most important, but not the only important one. It furnishes the bulk and that part of the coal in which the other constituents are held. The carbohydrates embrace the following:

1. Monosaccharides.
2. Disaccharides.
3. Trisaccharides.
4. Polysaccharides
   - Dextrosans (starch-dextrin-lichenin)
   - Levilosans
   - Mannans
   - Galactans
5. Gums
   - Gum arabic
   - Wound gums
   - Pentosans
6. Mucilages.
7. Pectins.
8. Celluloses
   - Hemi-celluloses
   - Normal celluloses
   - Compound celluloses
     - Pecto cellulose
     - Ligno cellulose
9. Cutin.
10. Suberin.

The carbohydrates differ greatly in the ease with which they are attacked by agencies of hydrolysis and decay. The mono-, di-, and trisaccharides are all water soluble and most of them are fermentable and food materials, but a few like talose and tagalose are entirely unfermentable. The polysaccharides must first be hydrolyzed before they can be fermented. They yield glucose on hydrolysis, which may be accomplished by dilute acids or by enzymes.

Gums

Gums are found in the wood of plants and trees, from which they often exude, as in the cherries and peach, corn stalks, straw, etc. On hydrolysis, the wood gums yield almost pure pentoses; they are therefore called pentosans. The wound gums yield arabinose; other forms of gum are gum arabic and gum tragacanth. The gums are hydrolyzed with difficulty, and for this reason are poor foods for animals and for micro-organisms.

Mucilages

Mucilages are secreted by certain hair-like organs on the skin of plants, leaves, and fruits. Their chemical composition is not known. When hydrolyzed, they yield arabinose, galactose and mannose.

Pectins

Pectins are commonly found in fruits, such as currants, gooseberries, apples, pears, etc., and in many fresh vegetables, like carrots, turnips, etc. They are easily soluble in hot water and when cooled set into jellies. The middle lamellæ of plant tissues are also composed of pectins. Pectine is hydrolyzable by acids forming glucose. It is also hydrolyzable by the enzyme pectinase secreted by micro-organisms. Gums and mucilages also form part of the tissues in wood and, as such, are important constituents.

Celluloses

Celluloses are by far the most important plant compounds to be considered. They are characterized by their greater insolubility and greater resistance to chemical reagents. They also differ greatly among themselves in this respect. Celluloses are classified into hemi-celluloses, normal celluloses, and compound celluloses.

Hemi-cellulose is found most abundantly in the cell walls of seeds, in the shells of nuts, rinds of fruits, seed coats of beans and peas, etc., and also form a small part of wood. They are more easily hydrolyzable than the other celluloses, and are thus separable from them.

Wood

In the ordinary leafy plants, as in herbs, shrubs, and trees, the actively living part of the plant is confined to the growing points, as in the tip of the roots and tips of the branches, and in a narrow zone between the bark and the wood of the stem in every part of the plant, called the cambium. In every case the growing point is the predecessor of the cambium in the stem. During the growing part of the year, the cells of the cambium divide actively in a plane parallel to the surface. The cells splitting off toward the outside form the cortex, or bark, those splitting off toward the inside eventually form the wood. In this manner the stems grow thicker. The new or young cells formed, whether in the growing plant or the cambium, at first consist of almost pure cellulose. But soon other substances are added to the cell wall besides cellulose from the protoplasm and the cell sap, consisting mainly of lignin, and small quantities of pectin, xylan, pentosan, and hemi-celluloses; later, still other substances are added mainly in the luminæ, such as tannins, phlobophenes, resins, waxes, fats, and a few other substances. The process is usually termed incrustation or lignification and the sum of the substances is called wood.

The resins, waxes, fats, and oils may be extracted by means of certain solvents, the tannins may be removed by boiling with water; the pectins and pectocellulose may be removed by hydrolysis with dilute acids by

boiling; the pentosans may be removed with dilute sodium hydroxide in the cold; see Table 1.[1] These processes leave the cellulose and the lignin intact, together called lignocellulose.

TABLE 1.—*Analyses of Woods*

(Results in Percentage of Oven-dry (105° C.) Samples)

Species	Moisture	Ash	Solubility in				
			Cold Water	Hot Water	Ether	1 Per Cent. NaOH	Acetic Acid
Western yellow pine...... (Pinus ponderosa)	6.42	0.46	4.09	5.05	8.52	20.30	1.09
Yellow cedar............ (Chamaecyparis noctkatensis)	4.89	0.43	2.47	3.11	2.55	13.41	1.59
Incense cedar........... (Libocedrus decurrens)	5.12	0.34	3.64	5.38	4.31	17.69	0.91
Redwood (heartwood).... (Sequoia sempervirens)	9.68	0.21	7.36	9.86	1.07	20.00	1.08
Western white pine...... (Pinus monticola)	7.00	0.20	3.16	4.49	4.26	14.78	1.03
Longleaf pine........... (Pinus palustris)		0.37	6.20	7.15	6.32	22.36	0.76
Douglas fir............. (Pseudotsuga taxifolia)		0.38	3.54	6.50	1.02	16.11	1.04
Western larch........... (Larix occidentalis)		0.23	10.61	12.59	0.81	22.14	0.71
White spruce............ (Picea canadensis)		0.31	1.12	2.14	1.36	11.57	1.59
Tanbark oak............ (Quercus densiflora)	3.66	0.83	4.10	5.60	0.80	23.96	5.23
Mesquite............... (Prosopis juliflora)	5.49	0.54	12.62	15.09	2.30	28.52	2.03
Balsa.................. (Ochroma lagopus)	6.47	2.12	1.77	2.79	1.23	20.37	5.80
Hickory (shellbark)...... (Hicoria ovata)	8.49	0.69	4.78	5.57	0.63	19.04	2.51
Eucalyptus............. (Eucalyptus globulus)	6.58	0.24	4.67	6.98	0.56	18.57	1.85
Basswood............... (Titia americana)		0.86	2.12	4.07	1.96	23.76	5.79
Yellow birch............ (Betula lutea)		0.52	2.67	3.97	0.60	19.85	4.30
Sugar maple............ (Acer saccharum)		0.44	2.65	4.36	0.25	17.64	4.46

[1] G. J. Ritter and L. C. Fleck: Chemistry of Wood. *Ind. & Eng. Chem.* (1922) **14**, 1050.

Lignocellulose

What relationship the cellulose and the lignin hold to one another is a much debated question by plant chemists. One school holds that the cellulose undergoes a transformation into lignin, and calls it the "transformation theory;" a second school holds that the cellulose and lignin are combined as esters, and calls it the "chemical theory;" a third school, and the oldest one, believes a condensation of the esterlike nature of cellulose with small quantities of pentosans and pentoses takes place, to which are added in an unknown way other substances, called lignin. To these theories must now be added that of Wislicenus,[2] called the "colloid-absorption theory." According to this idea, lignin is the sum total of the substances absorbed by the cellulose-fiber from the active cambium sap of the plant. Wislicenus holds that the cellulose and lignin are not combined chemically in any way but that they exist in the wood merely as colloidal mixtures. This theory does not preclude a chemical combination according to others.

The lignin and the cellulose in wood may be separated in two general ways: The lignin may be dissolved colloidally, leaving the cellulose undissolved, or the cellulose may be dissolved hydrolytically changing it to glucose and leaving the lignin undissolved. The lignin may be dissolved by treating wood with potassium chlorate; chlorine dioxide, boiling with phenol, caustic soda under pressure, sodium or potassium carbonate under pressure, and with acetyl bromide. The cellulose may be removed by hydrolysis with acids such as 70-per cent. sulfuric acid at room temperature, concentrated hydrochloric acid, 1-per cent. hydrochloric acid under pressure; gaseous hydrochloric acid; and glycerin-sulfuric acid mixture.

The amounts of cellulose and lignin obtained vary slightly with the methods used and widely in the different woods, age of the wood, whether sapwood or heartwood. Hardwood yields more than soft wood. Table 2 shows the quantities present in a number of woods.[3]

Cellulose

The plant chemist is completely in the dark concerning the chemistry of cellulose formation, but there are certain known facts that give a working hypothesis. The chemistry of the formation of starch is well understood. On hydrolysis, starch is degraded into glucose; cellulose likewise is degraded into glucose on hydrolysis. Although the relation

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[2] W. Wislicenus und W. Gierich: Beitrage zur Kolloidchemie der Zellulose. *Kolloid-Ztschr.* (1924) **34**, 169.

Wislicenus: *Kolloid Ztschr.* (1910) **6**, 87; (1920) **27**, 209.

[3] G. J. Ritter and L. C. Fleck: Chemistry of Wood. *Ind. & Eng. Chem.* (1923) **15**, 1056.

TABLE 2.—*Lignin and Cellulose in Various Woods*

Species	Sample	Per cent. Moisture	Per cent. Ash	Solubility in: Cold Water	Solubility in: Hot Water	Solubility in: Ether	Solubility in: 1 Per Cent. NaOH	Solubility in: Acetic Acid	Methoxyl	Pentosan	Methyl Pentosan	Cellulose	Lignin	In Cellulose: Pentosan	In Cellulose: Methyl Pentosan	In Cellulose: Alpha	In Cellulose: Beta	In Cellulose: Gamma
White ash:																		
No. 2 sapwood......	179	5.34	0.61	5.81	6.41	1.17	21.77	3.23	4.70	19.85	2.40	50.38	26.95	18.83	1.60	74.67	13.67	11.66
No. 2 heartwood.....	180	5.45	0.30	2.24	3.40	0.43	19.59	2.31	5.36	19.90	2.25	53.56	27.39	16.75	1.34	64.68	24.58	10.84
No. 3 sapwood......	181	4.91	0.57	5.25	7.02	0.88	21.93	3.70	5.66	20.16	2.63	49.72	27.39	19.67	1.60	55.11	28.29	16.50
No. 3 heartwood....	182	7.42	0.32	2.12	4.46	0.46	18.97	2.66	5.20	19.87	2.46	53.40	28.38	17.34	1.47	42.45	33.22	24.33
Yellow poplar:																		
No. 1 sapwood......	187	4.30	0.48	1.29	1.98	0.27	16.74	3.12	5.81	18.37	3.28	58.13	23.08	15.52	2.21	50.13	30.74	19.13
No. 1 heartwood....	188	3.79	0.39	1.50	2.08	0.43	17.70	2.89	5.86	18.47	3.11	59.57	22.19	14.97	2.40	61.30	20.20	18.50
No. 2 sapwood......	189	3.79	0.36	1.45	2.51	0.13	16.91	3.33	5.89	18.82	1.22	58.02	23.86	19.01	0.78	34.32	48.52	17.16
No. 2 heartwood....	190	3.88	0.33	1.45	2.89	0.58	17.57	2.73	6.03	19.08	1.13	59.47	23.69	17.83	1.47	36.67	42.75	20.58
Pignut hickory:																		
No. 1 sapwood......	191	3.54	0.40	4.91	6.45	0.29	19.11	3.58	5.56	18.18	1.11	56.08	21.87	16.90	1.30	51.55	21.92	26.53
No. 2 heartwood....	192	3.90	0.45	2.07	2.95	0.36	15.10	3.08	5.79	18.64	1.02	58.81	22.85	16.20	1.39	59.44	23.74	16.82
Yellow birch:																		
No. 1 sapwood......	207	4.92	0.26	1.05	1.98	0.48	16.77	2.34	5.66	21.36	1.66	58.91	24.69	20.72	1.13	52.15	32.90	14.45
No. 1 heartwood....	208	4.76	0.40	4.16	5.69	0.81	20.51	1.78	5.46	20.37	1.39	56.88	24.62	21.87	1.12	61.17	23.23	15.60
No. 2 sapwood......	213	4.28	0 18	1.74	2.10	0.88	19.78	3.75	5.47	22.30	1.82	56.57	27.76	22.19	1.71	52.40	26.82	20.78
No. 2 heartwood....	214	4.36	0.23	2.76	3.96	0.99	21.14	2.83	5.27	23.21	1.07	54.93	28.13	21.81	1.04	53.56	25.00	21.44
White oak:																		
No. 1 sapwood......	209	7.71	0.57	2.55	4.11	0.46	21.11	3.44	5.95	23.25	0.90	49.53	32.34	24.74	0.88	68.07	15.27	16.66
No. 1 heartwood....	210	7.70	0.43	7.33	10.15	0.71	25.81	2.59	6.18	21.82	1.57	48.68	32.74	24.22	0.58	67.33	11.84	20.83
No. 2 sapwood......	211	7.09	0.37	4.27	5.73	0.65	21.69	2.47	6.02	21.72	0.94	53.18	31.14	24.81	1.20	53.81	22.63	23.56
No. 2 heartwood....	212	6.99	0.42	4.76	6.60	0.62	22.67	2.97	5.64	22.08	0.91	52.12	31.30	24.54	0.96	52.96	20.41	26.63
Bald cypress:																		
No. 1 sapwood......	183	4.72	0.48	0.72	1.42	0.23	8.55	0.77	4.35	8.03	4.38	54.86	35.01	6.25	1.85	76.09	5.93	17.98
No. 1 heartwood....	184	5.30	0.30	2.79	2.99	4.87	10.59	0.48	3.94	6.67	4.49	53.10	33.06	5.84	1.80	76.83	3.94	19.23
No. 2 sapwood......	185	6.72	0.86	1.76	2.30	2.80	10.63	0.65	4.99	9.23	3.34	50.94	35.31	5.89	1.65	58.18	26.91	14.91
No. 2 heartwood....	186	4.72	0.95	3.27	3.49	7.93	13.56	0.29	4.07	7.88	3.36	49.18	32.27	6.33	1.25	57.38	24.75	17.87
White pine:																		
No. 1 sapwood......	193	3.90	0.23	3.55	5.15	5.46	17.16	1.68	4.16	9.31	2.14	54.25	26.51	6.81	2.09	54.56	17.47	27.97
No. 1 heartwood....	194	2.92	0.42	5.97	7.68	3.62	19.15	1.43	4.60	8.56	1.00	50.23	26.14	7.12	2.02	57.29	22.42	19.29
Yellow cedar:																		
No. 1 sapwood......	195	3.97	0.28	2.13	3.41	1.00	11.72	2.05	4.40	8.47	1.75	58.12	29.03	7.60	2.44	54.61	26.59	18.80
No. 1 heartwood....	196	4.00	0.18	2.88	4.12	1.32	12.77	1.53	4.81	8.69	1.85	56.08	28.73	7.78	2.73		20.17	
White cedar:																		
No. 2 sapwood......	197	5.59	0.64	2.18	2.82		11.02	1.17	5.07	11.61	0.94	55.77	29.85	10.35	1.77	73.78	0.99	25.23
No. 2 heartwood....	198	6.39	0.21	1.94	3.22		11.41	0.84	5.00	10.79	1.72	55.19	31.39	8.52	1.58	61.47	22.23	16.30
No. 3 sapwood......	199	6.02	0.48	3.02	3.96	1.44	12.71	1.11	5.23	10.82	1.16	55.02	32.14	8.95	1.28	69.17	14.04	16.79
No. 3 heartwood....	200	6.48	0.27	2.80	4.01	1.87	14.14	0.74	5.09	10.36	1.56	54.42	32.42	7.97	1.32	55.22	24.74	20.04
Incense cedar:																		
No. 1 sapwood......	205	6.46	0.47	1.92	2.97	0.67	11.16	1.33	5.95	12.08	0.45	49.09	34.73	10.14	1.24	50.69	12.98	36.33
No. 1 heartwood....	206	7.27	0.30	4.74	7.08	4.78	19.99	0.68	6.21	12.04	0.56	44.53	33.67	11.68	1.31	66.62	11.05	22.33

between cellulose and starch is not well enough known, it may be assumed that cellulose, like starch, is an anhydride of glucose;

$$C_6H_{12}O_6 - H_2O = C_6H_{10}O_5$$

It is therefore reasonable to assume that in the plant cellulose is also formed from sugar by splitting off water from glucose. There is a considerable difference of opinion as to whether the cellulose of all plants is the same. Most chemists hold that it differs slightly in different groups of plants. Heuser,[4] however, claims that there is only one type of cellulose and this is the same chemical individual in all plants.

Three types of decomposition of cellulose are recognized: namely, acid hydrolysis, decomposition by dry distillation, and decomposition by bacteria and fungi. Although each of these has great significance, the last is of the greatest importance, and it only can be considered here. That bacterial action upon cellulose leads to degradation is known by the gases, such as methane, carbon dioxide, and hydrogen, and fatty acids that result. These substances are the last metabolic products of a biochemical process. A number of micro-organisms are instrumental in the decomposition of cellulose, and according to the metabolic products resulting may be separated into four groups as follows:

1. Methane forming, produced by sewage bacteria, and bacteria in peat bogs giving methane, carbon dioxide, and the lower fatty acids ranging from formic to butyric acid.
2. Hydrogen forming, produced by *Bacterium fermentationis cellulosum,* giving hydrogen, carbon dioxide, and the lower fatty acids.
3. Methane-hydrogen forming, produced by thermophylic bacteria of different kinds, giving methane, hydrogen, carbon dioxide, formic acid, and acetic acid.
4. Nitrogen forming, produced by denitrifying bacteria, forming nitrogen and carbon dioxide, and nitrogen assimilating bacteria, taking up nitrogen from the and air requiring cellulose for their carbon supply.

The active agents of decomposition are the enzymes secreted by the micro-organisms. As in all carbohydrate decomposition, two groups of enzymes are necessary for the decomposition of cellulose; those causing hydrolysis and those causing fermentation. Hydrolysis precedes fermentation, but the two proceed simultaneously. Through hydrolysis, by means of the enzyme cellulase, cellulose is decomposed first into cellobiose; and cellobiose is then changed into glucose by means of the enzyme cellobiase. Only after the glucose has been formed does fermentation set in. In this, a number of kinds of bacteria may take part, resulting in the products named above according to the conditions and the type of bacteria involved. Zymase is the enzyme active in this process.

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[4] Emil Heuser, Clarence J. West, and Gustavus Esselen: "Textbook of Cellulose Chemistry." McGraw-Hill Book Co., 1924.

Lignin

In spite of the large amount of work done on lignin, it is impossible to give it a precise definition. Considering all the results obtained through chemical investigations, it must be concluded that lignin is not a unit or individual substance, and cannot be expressed by a definite formula. Many attempts have been made to give an empirical formula expressing its composition, but hardly any two investigators have arrived at the same formula. As to its constitutional formula, only a few suggestions have been attempted. Chemistry so far has failed to reveal its true constitution.

Different investigators obtain slightly different results in the elementary analysis of lignin. The carbon content is considerably higher in lignin than in cellulose. Table 3 shows the composition of lignin:

TABLE 3.—*Analyses of Lignin*

Investigator	C, Per Cent.	H_2, Per Cent.	O_2, Per Cent.	OCH_3, Per Cent.
Fischer and Schrader[a]	64.89	5.68	29.53	13.10
Hägglund[b]	65.47	5.47	29.09	14.79
Goldschmidt[b]	62.70	5.17	32.13	
Klason[b]	63.97	5 32		13.19
Beckman, Liesch and Lehman[b]	62.92	5.78	31.60	15 81

[a] Franz Fischer und Hans Schrader: Ueber die Trockene Distillation von Lignin und Cellulose. *Gesamm. Abh. z. Kenntnis d. Kohle* (1920) **5**, 106.

[b] R. Riefenstahl: Der Gegenwärtige Stand der Lignin Chemie. *Zeit. f. angew. Chemie.* (1924) **37**, 169.

As to the constitution of lignin, it is assumed from one side that lignin is of an aromatic nature; this is denied by others. It has been proved that the lignin molecule contains a methoxyl (OCH_3) group, the source of alcohol in lignin and in wood. The amount of methoxyl is shown in Tables 2 and 4. An acetyl group has also been shown to be present. Further it is claimed to have several (two or three) hydroxyl groups, a carboxyl $\left(C \begin{matrix} \nearrow O \\ \searrow OH \end{matrix} \right)$ group, and a ketone group.

The decomposition of many substances through various agencies may be followed step by step and the products determined at every step, thus affording a fair knowledge of the composition of the original substance. In lignin, this has not been possible and little has been learned in this manner. Yet the products obtained through various agents of decomposition and the behavior of lignin during the processes have furnished valuable data as to its nature.

TABLE 4.—*Ratio of Methoxyl to Lignin in Oven-dry (105° C.) Weight of Wood* [a]

Species	No.	Lignin Sapwood	Lignin Heartwood	OCH_3 Sapwood	OCH_3 Heartwood	$\frac{OCH_3 \times 100}{\text{Lignin}}$ Sapwood	$\frac{OCH_3 \times 100}{\text{Lignin}}$ Heartwood
White ash	2	26.95	27.39	4.70	5.36	17.4	19.5
	3	27.39	28.38	5.66	5.20	20.0	18.3
Yellow poplar	1	23.08	22.19	5.81	5.86	25.2	26.4
	2	23.86	23.69	5.89	6.03	24.7	25.4
Black hickory	1	21.87	22.85	5.56	5.79	25.4	25.3
Red alder	1	25.97	25.68	2.29	5.33	20.4	20.1
	2	26.64	25.94	5.26	5.26	19.8	20.3
Bald cypress	1	35.01	33.06	4.35	3.94	12.4	11.9
	2	35.31	32.27	4.99	4.07	14.0	12.6
Eastern white pine	1	26.52	26.14	4.16	4.60	15.7	17.6
Yellow cedar	1	29.03	28.73	4.40	4.81	15.1	16.7
Southern white pine	2	29.85	31.39	5.07	5.00	17.1	15.9
	3	32.14	32.42	5.23	5.09	16.2	15.7
Incense cedar	1	34.73	33.67	5.95	6.21	17.1	18.4

[a] G. J. Ritter and L. C. Fleck: Chemistry of Wood. VII, Relation between Methoxyl and Lignin in Wood. *Ind. & Eng. Chem.* (1923) **15**, 1264.

The lignin molecule may be decomposed by heating with alkalies, by strong reducing agents, and by oxidizing agents. The decomposition products may be separated into those that indicate an aromatic character, like phenol, quinone, vanillin, protocatechuic acid, and pyrocatechin; and such products as indicate an aliphatic character, like succinic, malonic, acetic, formic, oxalic and adipic acids. Furfural is claimed to have been found by some chemists, but its presence is doubtful.

When lignin is subjected to fusion with potassium, it results in a humin-like substance, from which may be separated protocatechuic acid, pyrocatechin, vanillin, and adipin in varying but small proportions, according to the conditions imposed upon it. Oxalic acid may be separated in rather large quantities, as high as 20 per cent. Lignin is not attacked by weak reducing agents and energetic reagents like zinc dust, iodic acid and phosphorus at higher temperatures must be employed. The products are hydro-aromatic hydrocarbons of unknown composition. On the other hand, oxidizing reagents, like ozone, hydrogen peroxide, potassium permanganate, hydrochloric acid, and chlorine dioxide, decomposed lignin easily, resulting in decomposition products of low molecular weight that give no clue as to its constitution. According to the reagents used and conditions imposed, varying quantities of oxalic acid, carbon dioxide, water, formic, acetic, and succinic acids are obtained.

The main product is oxalic acid; as much as 20 per cent. of oxalic acid was found.

The products obtained from lignin by dry distillation depends, as with other substances, on the conditions of heating. On heating it to 500° C., Heuser and Skiöldebrand obtained 15.8 per cent. tarry water, 13.0 per cent. tar, and 50.6 per cent. carbon. Fischer and Schrader report 10.2 to 13.9 per cent. water, 12.3 to 14.4 per cent. tar, 15.8 to 19.2 per cent. gas, and 57.0 to 57.2 per cent. coke.

The gases consist of carbon dioxide, carbon monoxide, methane, and a hydrocarbon C_nH_{2n}. Noteworthy is the low carbon dioxide and the high carbon monoxide and methane.

The watery distillates are composed of water, acetic acid, acetone, methyl alcohol, and perhaps vanillinic acid.

The tars consist of 13 per cent. neutral substances, 34 per cent. phenols, 16 per cent. acids, and 37 per cent. water-soluble organic substances.

Calculated for the original lignin we have 1.6 per cent. neutral constituents, 4.2 per cent. phenols, and 2.0 per cent. acids.

Lignin is attacked but slowly by bacteria and fungi. Little, however, is known in this respect. Most fungi do not attack lignin when inoculated. A few fungi, however, one in particular, *Trametes pini*, will attack lignin in wood but not the cellulose.

Bark

Bark is a very complex substance, consisting chiefly of bast fibers and cork. The composition of cork is also complex, and a number of complex substances, like phellonic acid, an alicyclic compound, phloic acid, and suberic acid, have been isolated from it. A large number of other complex substances have been isolated from various corks. The main substance in cork is suberin. Its composition is not known, but it is said to be similar in composition to fats and waxes.

Cuto-Cellulose

The term cuto-cellulose is applied to covering membranes or cutins of plants; their composition is not well known. Recent investigations show that they consist of esters of glycerin and fatty acids, and esters of higher alcohols and fatty acids, mixed with free fatty acids, and alcohols and other substances. Cuto-celluloses form the principal protective tissues. They are very resistant to oxidation and weathering, and to bacterial and fungal agencies.

It was assumed for a long time that the so-called cuto-cellulose was a combination of fatty, waxy and resinous substances with cellulose. Recent investigations[5] show that no cellulose is present in the compound.

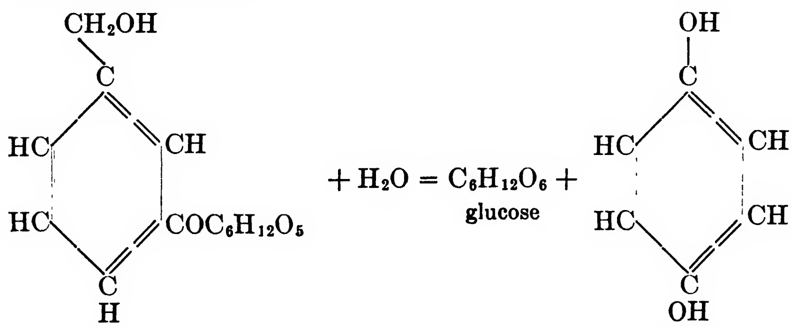
[5] Roscoe W. Thatcher: "The Chemistry of Plant Life." McGraw-Hill Book Co., New York, 1921.

Glucosides

Glucosides are ethers of some monosaccharide, usually glucose, with some closed-ring benzene derivative. They are very common and universally present plant compounds. There are a number of types, such as phenols, alcohols, aldehydes, acids, oxyflavons, anthraquinone, nitriles, pigment, etc., embracing a large number of glucosides. The following are a few of the well known: arbutin, digitalin, hesperidine, quercitin, salicin, cyanin, coniferin, malvin, populin, indicein, amygdalin, apein.

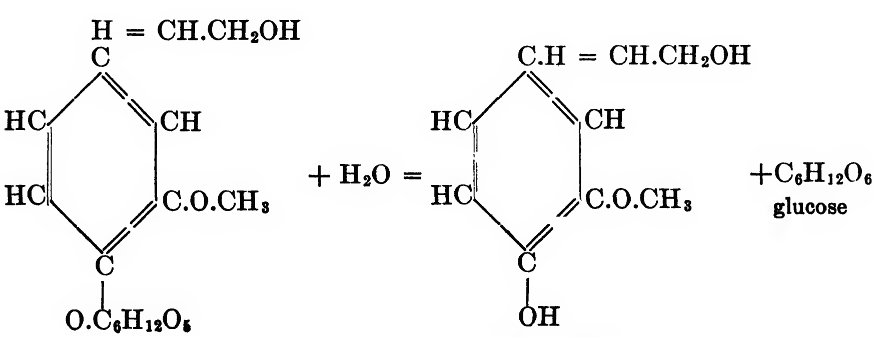
The natural glucosides are hydrolyzed readily by boiling with dilute mineral acids, and easily by enzymes that occur in the same plant tissues but in different cells: The primary products of hydrolysis are glucose, or in some cases some other monosaccharide, and some closed-ring benzene derivative. A large number of enzymes have been isolated, many of which will hydrolyze only one specific glucoside. Micro-organisms are able to hydrolyze glucoside in a similar way by means of enzymes. The hydrolysis of the following glucosides shows at once their structure and the typical reactions:

1. Arbutin, $C_{12}H_{16}O_7$

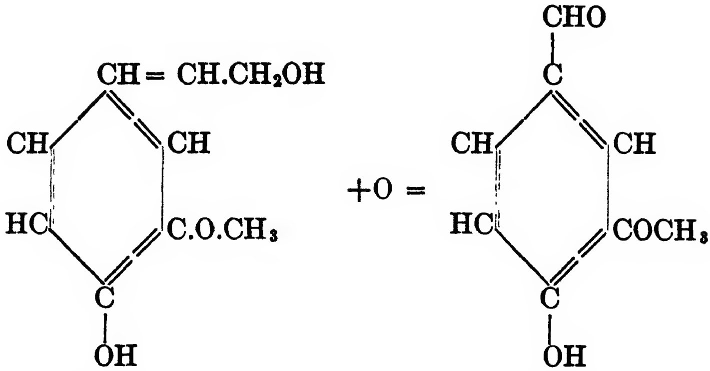


arbutin hydroquinone

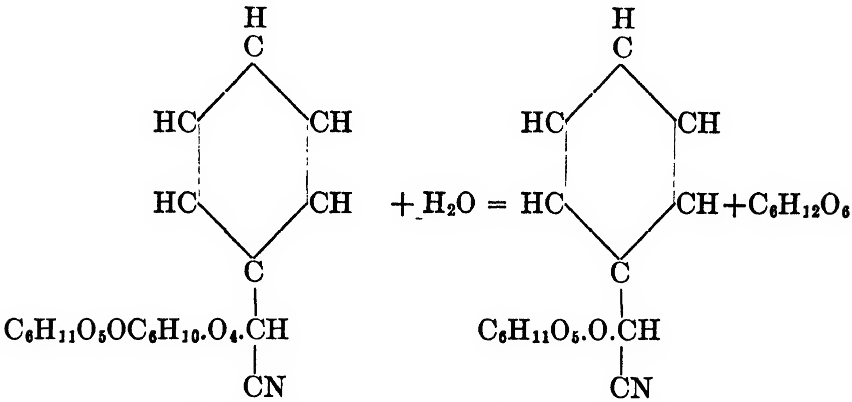
2. Coniferin, $C_{16}H_{22}O_8$



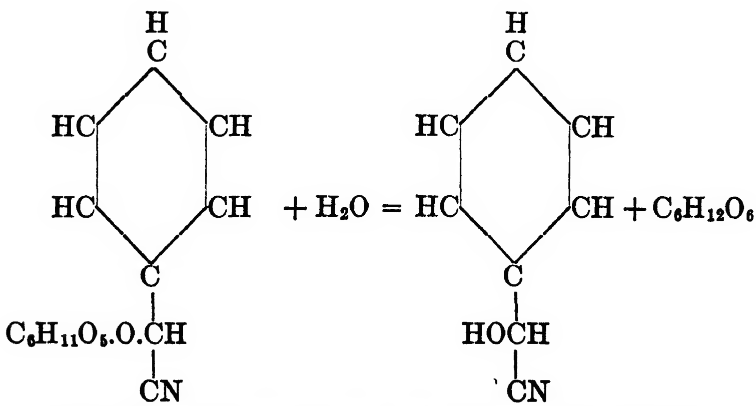
coniferyl alcohol



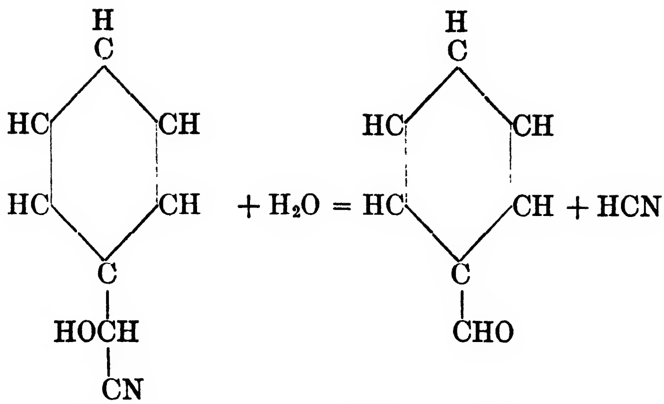
coniferyl alcohol vanillan



amygdalin + water = mandelonitrile glucoside + glucose



mandelonitrile glucoside + water = mandelonitrile + glucose

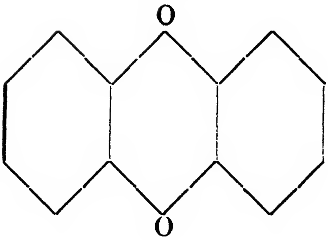


mandelonitrile + water = benzaldehyde + hydrocyanic acid.

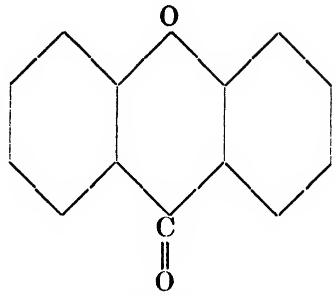
These examples of reactions and structure are sufficient to show their general nature. The sugars resulting from the splitting are foods for both bacteria and fungi and are quickly decomposed. The benzene derivatives are not further available as food for organisms of decay, and must contribute to the deposit, absorbed by the woody degradation matters. Some of these have been found in peat and in rotten wood, and are responsible for the peculiar odor in rotten wood. Vanillin, for example, is a constant substance in both rotten wood and peat. When coal is dissolved by means of Schulze's reagent, the smell of rotten wood is pronounced. The disposal of the glucoside in peat is yet a closed book.

Of particular interest are the pigment glucosides, as they are the possible mother-substances of the dye substances found in coal tars. These are probably the most general and universally present of the glucosides. To be assured of this, one has only to look around and observe the different colors in plants other than green, particularly in the fall. Most, if not all of the red, yellow, blue, and violet are due to these glucosides.

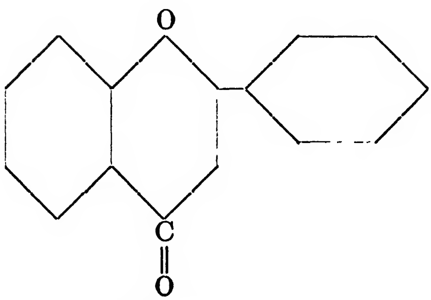
There are four basic types of these glucosides: those with the anthraquinone nucleus, giving rise to the alizarine reds; those with the zanthone nucleus, the yellows; those with the flavone nucleus, also the yellows; and those with the anthocyan nucleus, giving rise to the interchangeable soluble red, blue, and violet colors. They are all of the condensed benzene ring type, two rings being united by a third, in which there are either two atoms in the ring and one atom and a second attached to the opposite carbon in the (C = O) arrangement.



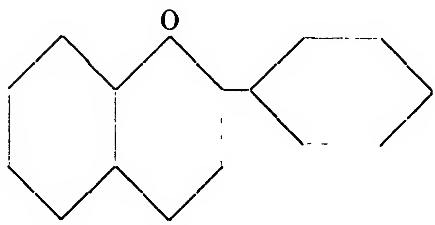
Anthraquinone



Xanthone



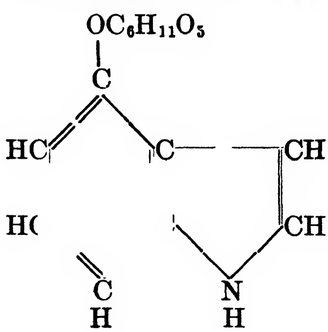
Flavone

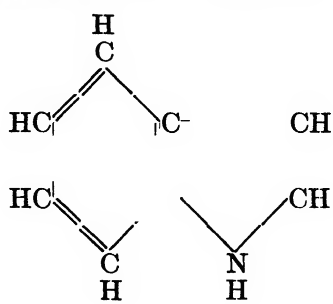


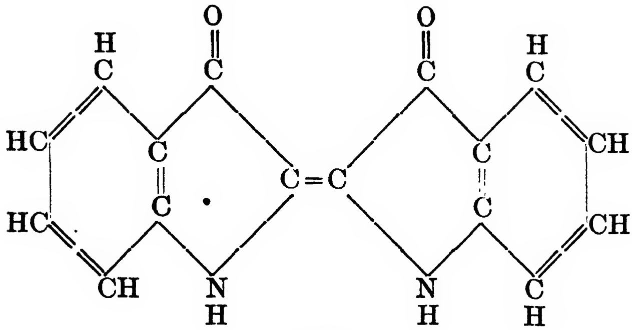
Anthocyan

Indican also belongs to the pigment glucosides, but its constitution is of an entirely different type. The glucoside hydrolyzes to indoxyl, and this is easily oxidized to indigo, the important dye.

Indican			Glucose		Indoxyl
$C_{14}H_{17}O_6N$	+	H_2O =	$C_6H_{12}O_6$	+	C_8H_7ON







Indigo

Tannins

Tannins are either free phenol acids, or more often glucosides of these acids. Common tannin yields 7 to 8 per cent. of glucose on hydrolysis. Each glucose molecule has five phenol acid groups attached to it. Tannins also are common and universal plant products. Barks, as well as many leaves, are particularly rich in tannins.

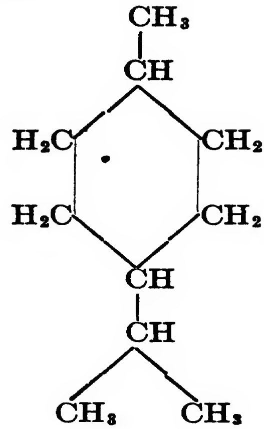
Essential Oils

Terpenes and Camphors.—Terpenes are important substances in consideration of the constitution of coal. They are common plant products, frequently associated with the resins. Resins and balsams are often the solutions of resinous acids in terpenes. The conifers are particularly characterized by secreting large quantities of terpenes, but many other plants are also rich in terpenes and essential oils. Like the resins, they are found in special cells, ducts, and reservoirs in the wood, bark, and leaves. They behave as unsaturated compounds, and are almost all oils of high boiling points. They volatilize without decomposition in steam, polymerize easily, and reorganize on heating slightly. When exposed to the air, they oxidize and harden. They are not decomposible through micro-organisms. Many of them are bactericides and are used as disinfectants. Several different types are recognized as follows:

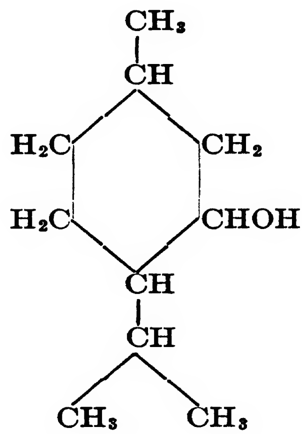
Hydrocarbon oils or terpenes	Hemiterpenes = C_5H_8 Monocyclic = $C_{10}H_{16}$ Bicyclic = $C_{10}H_{16}$ Polycyclic = $(C_5H_8)_n$ Hydroterpenes = $C_{10}H_{18}$ and $C_{10}H_{20}$
Oxygenated and sulfuretted	Oxygenated, usually called camphors = alcohol, ketones, aldehydes, acids, esters, or phenol derivatives of the former. Sulfuretted oils

The following are common examples:

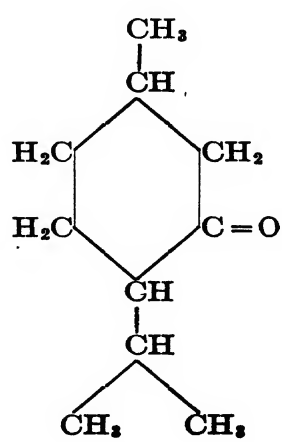
Menthane $C_{10}H_{20}$
(hydrocarbon)



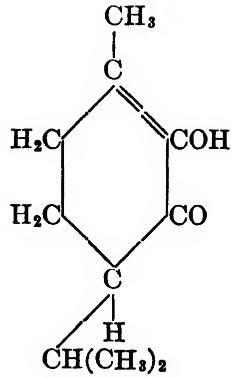
Menthol ($C_{10}H_{20}O$)
(alcohol)



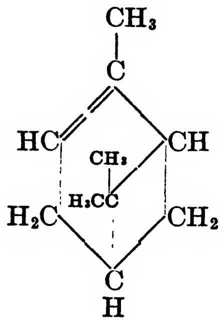
Menthone ($C_{10}H_{18}O$)
(ketone)



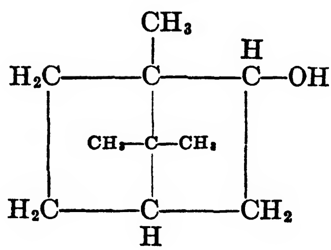
Buccocamphor ($C_{11}H_{16}O_2$)
(ketophenol)



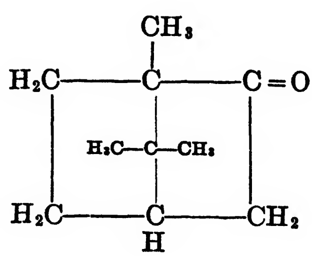
Bicyclic pinene $C_{10}H_{16}$
(hydrocarbon)



Borneol $C_{10}H_{17}OH$
(alcohol)



Camphor $C_{10}H_{16}O$
(ketone)



Resins.—Like the terpenes, resins are deposited as a waste matter in the wood, bark, and leaves of many plants, but most abundantly in the conifers. They are stored in and held in special vessels, the resin vessels, schizogenous cavities or pockets and canals. Many often appear as a

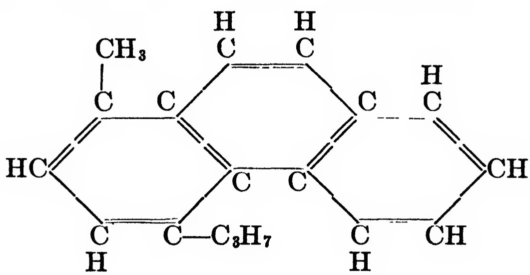
viscous solution in terpenes, called balsams and turpentines. Their mode of formation is not known.

When dried they are amorphous, brittle, yellow-brown substances. At first, they may be but lightly colored or colorless; but when exposed to the air, they often harden and assume a dark-brown color through volatilization of the terpenes, but primarily to oxidation becoming solid substances.

Chemically considered, they are composed of a mixture of resinous alcohols and phenols, partly free and partly in the form of esters with resinous acids or other acids. The amount of free acids is variable; some resins are composed almost entirely of free acids. Specific components of resins are: Resinic acids or resinole acids, resinic alcohols or resinols, resinic phenols, resinic phenols with tannin characters or resinic tanols, resenes. As far as they are known, they are ring and conjugated-ring compounds and their derivatives. Terpenes are present more or less as solvents. With these mixtures many other substances may be present.

The resins are insoluble in water and acids, but easily soluble in organic solvents, like ether, benzol, alcohol, and chloroform. They may be more or less completely saponified by alkalies, and are not subject to bacterial decomposition.

Resinic Acids.—Although the chemistry of the resinic acids is still incomplete, they are better understood than the other components of the resins. They are soluble in alkali carbonates. They are probably related to the terpenes. It has been shown by Tschirch[6] that retene is formed when resinic acids of conifers are distilled; and Vesterberg[7] has succeeded in converting abietinic acid into retene. This leads to the belief that they are derivatives of retene ($C_{18}H_{18}$)



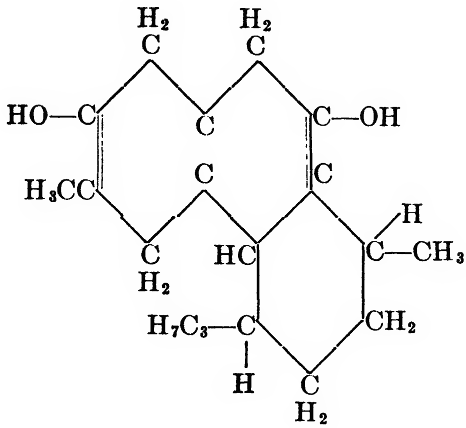
The same residue is found in fichtelite, a fossil resin.

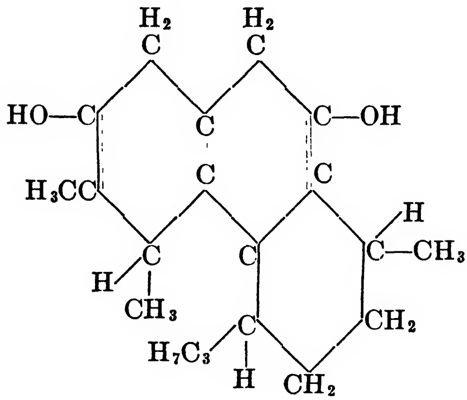
Different plants do not contain specific acids. In other words, specific acids are not characteristic of certain plants, but are found in mixtures of related forms that will differ not only in different kinds of plants, but also in the same plant under different conditions and at different times of the year. They are not stable, are sensitive to heat exposures; and are

[6] A. Tschirch: Die Harze. Gebr. Borntrager, 685. Leipzig, 1906.

[7] A. Tschirch: *loc. cit.*

easily oxidized. They are optically active. The best known are abietinic acid and pimaric acid.





Resinoles.—The resinoles are crystallizable; their character is partly that of phenols, and partly that of alcohols. The best known is amyrin, $C_{30}H_{49}OH$, a triterpin, found in elemi resin.

Resino Tanols.—The resino tanols are amorphous, aromatic alcohols, with characters of tannin. When distilled they yield aromatic hydrocarbons, and when oxidized with nitric acid they form picric acid. The resenes are but little known.

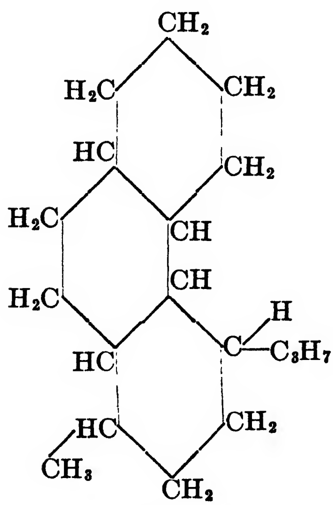
Fossil Resins.—The study of fossil resins sheds considerable light on the resins in coal. Like resins, fossil resins are complex compounds and often mixtures of compounds. Amber is the general expression for a fossil resin. But amber, like resin, is not a specific term for a specific substance, but is a collective name for a number of substances or mixture of substances. More precise names for fossil resins are succinite and fichtelite, the best known of a long list. Succinite is the resin found in

fossil pines, *Pinus succinifer* and *Pinus sylvatica, Pinus Baltica* and *Pinus cembrifolia.*

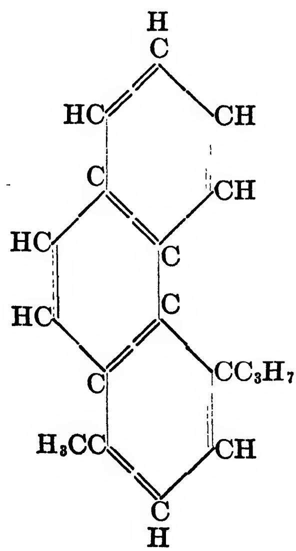
Succinite has been the object of a series of investigations over a considerable time. The great difficulty in its investigation lay in its difficult solubility in all solvents. After many months of treatment with alcohol in a reflux condenser, only about 30 per cent. was soluble. This part was found to consist of borneol and succino-abietinic acid. The borneol amounted to 2 per cent. and succino-abietinic acid 28 per cent. of the total succinite. Being found in many conifers, it is assumed that borneol and abietinic acid are present as an ester.

The remaining 70 per cent. was not completely soluble in all known solvents, none having the least effect on it except chloroform and carbon disulfide, which caused it to swell considerably, but dissolved but very small quantities after days of boiling. After repeated renewal 0.5 per cent. of alcoholic potassium dissolved 7.8 per cent., which proved to be succinic acid. After further treatment with alcoholic potassium, the remaining residue proved to be a resinole, $C_{12}H_{20}O$.

Fichelite is another substance that gave up its secrets only after repeated attacks of a number of investigators over a considerable number of years. It withstood every attempt to split the molecule step by step. It was finally shown to be a perhydrate of retene: $C_{18}H_{32}$.

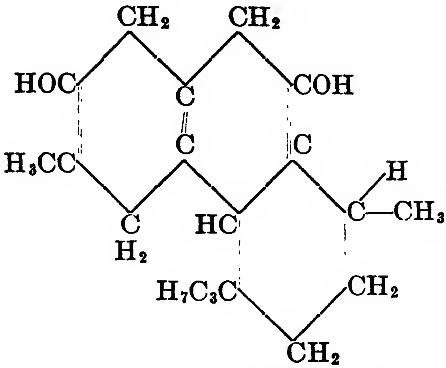


Fichelite



Retene

Abietinic acid, $C_{18}H_{28}O_2$, which has a similar structure, has been changed into retene.



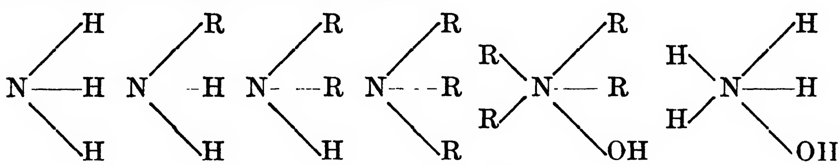
Abietinic acid

Vegetable Bases

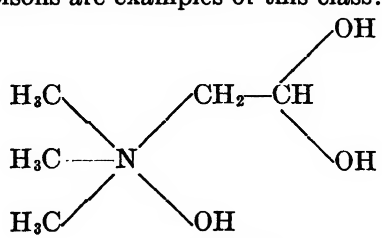
In the vegetable bases, we find characteristically nitrogenous compounds of plants. They may be divided into three groups: Plant amines, which are simple open chain compounds; alkaloids—simple closed ring compounds, including a nitrogen atom in the ring; purine bases—complex compounds containing a nucleus with four nitrogen atoms arranged alternately to form a double ring.

Amines

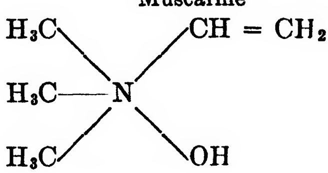
The simple amines may be considered to be derived from ammonia or ammonium hydroxide as follows:



The ptomaine poisons are examples of this class:

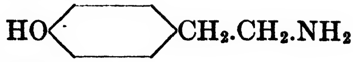


Muscarine



Neurine

Phenyl derivatives are also found, like

hydroxyphenylethylamine: 

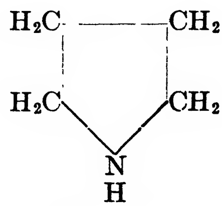
and hordine : 

These, however, are probably of no great importance as mother substances of nitrogen in coal, because on hydrolysis the nitrogenous product would further decompose to ammonia.

Alkaloids

Alkaloids are vegetable bases whose nitrogen is part of a heterocyclic closed-ring arrangement. They are insoluble in water. They may be grouped according to their structure into the following groups:

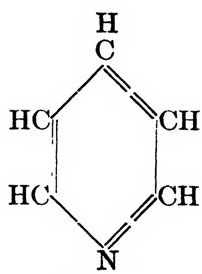
Pyrrolidine group:



Pyrrolidine

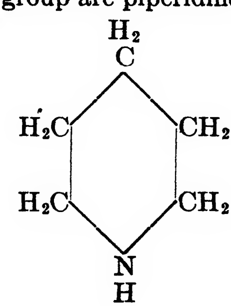
Other members of the group are stachydrine and hygrine.

The pyridine group:

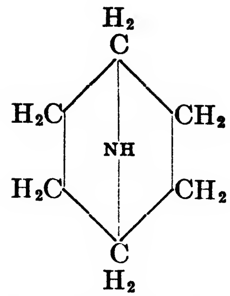


Pyridine

Other members of this group are piperidine, nicotine, and conine:

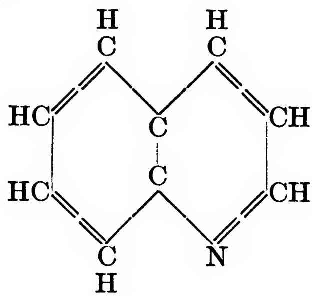


The tropine group:



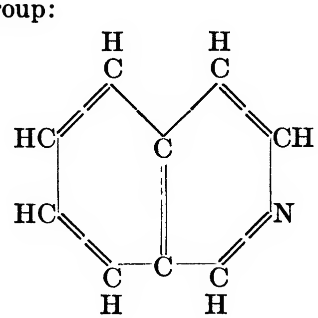
Cocaine and atropine also belong to this group.

The quinoline group:



to which also belong quinine, strychnine, and cinchonine.

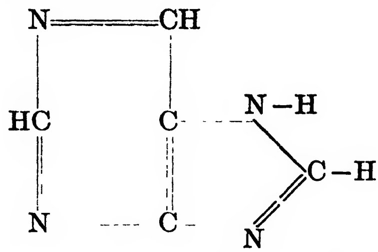
The isoquinoline group:



to which also belongs morphine with a very complicated structure. Some alkaloids are composites of two or more of these groups, like nicotine, which is a combination of pyrridine with a pyrrolidine nucleus. A large number of alkaloids are now known.

Purine Bases

Purine bases are widely distributed in plants. They may all be thought of as being derived from purine:



To this class belong, among many others: xanthine, uric acid, guanine, theobromine, theophylline, and caffeine.

Biochemical Decomposition

A knowledge of the chemistry of plants alone will add but little to a comprehensible knowledge of what the plants contribute to coal, because plants did not contribute their products in their original state nor did all remain to contribute. Long before the real coalification processes began, the contributing plant matter was subject to a drastic biological transformation—in brief, decay. Before going any further, we must inquire more thoroughly into the question as to what is decay, what is the mechanism of decay, and what are the results and products.

Decay

Micro-organisms require food for building up their bodies and to supply energy. The sum of the changes going on in the body is called metabolism. Metabolism consists of several separate functions: the building up of the body, called anabolism; the deterioration or tearing down, called katabolism; and the most important one, to supply energy, called respiration or fermentation. The last function is well known and may be produced in the laboratory without micro-organisms. The processes of katabolism are partly known, while anabolism or the synthetic processes are known but very little. Many organisms live upon cellulose, starch, fat, gelatin, keratin, and other water-insoluble foods. But their life processes depend on water-soluble foods, or foods that will diffuse into the cell wall and come in contact with the protoplasm where all metabolism takes place. But as insoluble foods do not diffuse into the cell and the protoplasm cannot diffuse out, the insoluble foods must first be transformed into soluble ones. This the organisms accomplish by secreting substances that will split the insoluble foods into soluble parts. The substances that bring about these transformations are called enzymes. The soluble compounds thus formed can then diffuse into the cell of the micro-organism, where they are digested or fermented, by the aid of other enzymes, and yield the energy for the cell, and build up the cell. Many kinds of enzymes are known, each one acting in a specific way on a specific substance. It

will be seen then that the process involves two definite stages: food preparation, and digestion or fermentation, also called respiration. The insoluble foods often are broken down step by step before they are actually ready for the final step. This is well illustrated by fungi living on starch. Starch is first changed by means of the enzyme diastase to maltose; maltose is split by maltase to glucose; glucose diffuses into the cell where it is finally changed by the aid of zymase to alcohol and carbon dioxide. This last change is the vital one; it furnishes the energy required. The first steps are preparatory. The organism could live equally well on maltose, in fact, more economically. Another example is found in bacteria living on cellulose, as already noted. These secrete the enzyme cellulase. Cellulase changes cellulose first into cellobiose and cellobiose is then changed by the enzyme cellobiase to glucose, glucose is diffused into the cell where it is fermented by means of the enzyme zymase to alcohol and carbon dioxide or the glucose may be changed into other substances. The last stage furnishes the energy. It cannot live on alcohol and carbon dioxide.

It must not be thought that decomposition of starch and sugar is always as simple as given in the examples. To discuss the various ways in which the sugar, starch, and other carbohydrates may be decomposed would go too far for this purpose, and cannot even be outlined here. Besides alcohol and carbon dioxide, organic acids are also formed in certain cases. The organic acids and alcohols can be decomposed further by both bacteria and fungi, and by some yeasts, to simpler compounds. Ordinarily, this decomposition consists in complete oxidation. The acids are completely oxidized to carbon dioxide and water. Alcohol is first oxidized to acetic acid, and this to carbon dioxide and water.

The discussion and example just given plainly show two kinds of reactions. The one is hydrolytic and the other fermenting or respiratory. Besides these in bacterial decomposition, two other groups are distinguished; namely, oxidizing and reducing.

Enzymes may therefore be classified as follows:

Hydrolytic enzymes:

1. Of carbohydrates: cellulase or cytase, diastase or amylase, invertase, lactase, maltase.
2. Of fats: lipase.
3. Of proteins (*a*) proteolytic: pepsin, trypsin, erapsin; (*b*) coagulating: thrombase, rennet.
4. Of glucosides: emulsin.

Zymase or fermenting enzymes:

1. Of carbohydrates: zymase, lactacidase.
2. Of other nitrogen-free bodies: vinegar—oxidase.
3. Of proteins: endo-tryptase, amidase, urase.

Oxidizing enzymes:

1. Oxidase, tyrosinase.

Reducing enzymes:

Catalase, reductases of nitrates, sulfur, sulfates, etc.

Probably all micro-organisms produce several to many enzymes. As was shown before, several are necessary to decompose a substance hydrolytically before it can ferment; diastase changes starch to maltose, maltase changes maltose to dextrose, and finally the Zymase changes dextrose to alcohol and carbon dioxide. The number of enzymes in some organisms is large. It has been found that Aspergillus nigar and Penicillium camenberti produce almost all the enzymes that have ever been found. Many organisms live on the products of others; this is called symbiosis. In some bacteria, a symbiotic relationship is absolutely essential.

The two terms hydrolysis and respiration or fermentation cover all the principles underlying decay. The term putrefaction is often used, particularly when decomposition is accompanied by fetid odors. As bad odors are due to certain sulfur compounds and as these can only be formed from organic substances containing sulfur, like the proteins, putrefaction has come to mean protein decomposition. The statement is sometimes also made that putrefaction is caused exclusively by anaerobic bacteria. It was first used by Justus Liebig in this sense. This is incorrect, as both aerobic and anaerobic bacteria are instrumental in proteolitic decomposition, in fact aerobic more generally than anaerobic.

Types of Bacteria and Fungal Decay

In the previous section was described the mechanism of decay by bacteria and fungi, but it is also of great importance to take into consideration the types of bacterial and fungal decay.

We have already seen that plants alone can manufacture carbohydrates, by means of a process called photosynthesis with the aid of chlorophyl and light. From the carbohydrates, the plants manufacture further proteins, by the addition of an NH_2 group obtained from nitrates in a manner as yet unknown. As in bacteria, this process of building up is called anabolism. The plant also carries on other life functions, that of tearing down, called katabolism. By this process, many other plant products are formed, usually termed waste products, already mentioned. All the functions of the plant taken together are called metabolism, and produce the plant with all there is to it, the plant as a whole. Animals depend solely on plants for their existence, and the few changes that occur from plants into animals may be ignored for the purpose of this study.

With few exceptions plants, together with that part transformed into the animal body, constitute the organic matter on earth. All

organic matter is undergoing continuous changes. Organisms not only grow, they also decompose. The same carbon, hydrogen, oxygen, nitrogen, and sulfur molecules that chiefly constitute the organic world of today, constituted it as long as life has existed. While green plants build up the organic compounds, the bacteria destroy them. Without bacteria, the world would soon be filled with undecomposed organisms and new life would soon be impossible. The substances that compose even organisms therefore go through cycles, as discussed in the following section.

The Carbon Cycle.—Carbon is the most important element in life. Beginning with the simplest compound, carbon dioxide of the air, it is absorbed by the green plants and is changed, together with water, into carbohydrates, like sugars, starch, cellulose, lignin; or into fats, acids, and to protein on further addition of nitrogen from nitrates, and sulfur from sulfates, and to other substances. The plants will either die and decay, or be eaten by animals that die and decay. Both plants and animals are decomposed step by step, until finally returned to carbon dioxide and water. Even methane, alcohol, and the toxic compounds, as morphine, nicotine, and others, are eventually returned by bacterial action to the elements.

Both hydrogen and oxygen are so closely linked with the carbon atom that they may be said to go through the same cycle with the carbon atom. In fact, in most cases, it is the oxygen atom the bacteria are after.

The Nitrogen Cycle.—Nitrates in a large measure, and ammonia to some extent, constitute the sources of nitrogen of the higher plants, which transform them into amino acids, amides, and proteins by combining the NH_2 ion derived from them with carbohydrates previously manufactured by the plants from carbon dioxide and water. Leaving out of consideration the part played by animals that live on plants, there are eight or nine well-known phases of transformation of nitrogen by micro-organisms:

Protein decomposition.

Ammonia formation.

Nitrification.

These three constitute the normal steps in the mineralization of nitrogen and are the counterpart of the processes performed by the higher plants.

Reduction of nitrate to nitrite and ammonia

Assimilation of amino and ammonia.

Assimilation of nitrate nitrogen to proteins.

These three constitute the retrograde changes and are in competition with higher plants.

Denitrification or liberation of nitrogen from nitrates or nitrites.

The oxidation of ammonia to free nitrogen and water.

Fixation of free nitrogen.

Decomposition of Proteins.—Because of the varied compositions of proteins, their decomposition varies considerably and ends in widely differing results. The processes are but little known. A large number of molds, yeasts, bacteria, protozoa, and other organisms are always at hand to attack any protein substances as soon as the death of a plant or animal sets in and the factors that check bacterial activities disappear. Aerobic and anaerobic, psychrophilic and thermophilic organisms may be active. A considerable number of different kinds of enzymes are active in this transformation. The first decomposition products are formed through hydrolysis, the same as in carbohydrate decomposition. The amino acids are the first well-known compounds of protein decomposition; other products are the amides.

Formation of Ammonia.—From here on decomposition proceeds through a large number of intermediary compounds, some of them with very disagreeable odors. The end product of the nitrogen-containing fragment is always ammonia.

Besides the proteins, there are a large number of other nitrogenous compounds in plants and animals, like chitin, quinine, strychnine, morphine, nicotine, etc., and all of these are eventually decomposed and the nitrogenous fragments resulting are composed of ammonia. It must be understood, however, that the various compounds do not decompose with the same ease. Those that generally serve as foods are very easily decomposed; those that function in protection or are waste products decompose with difficulty; and those that are classed among the toxins decompose only under special conditions.

Nitrification.—It is said that the last fragment of protein decomposition, as well as that of other nitrogen compounds, is ammonia. Ammonia may further be transformed into nitrite, through an oxidation process by means of nitrite bacteria. Nitrate bacteria then completes the oxidation of nitrite to nitric acid. Basic substances that may be present will then neutralize the acid, forming nitrates. The nitrates are then again available for plants. The nitrite and nitrate formation proceeds simultaneously in the soil. As a rule, the presence of organic substances is favorable to the nitrifying organisms; and the more humus there is present in the soil the more active are the organisms. In peat bogs, however, nitrifying organisms are not active. In these, there are not enough basic compounds necessary to neutralize the nitric and nitrous acids formed and not enough oxygen to permit rapid oxidation.

Nitrate Reduction.—There is a large number of bacteria that perform the opposite transformation and reduce nitrates to ammonia. Two steps are necessary in some cases, one set of bacteria reducing to nitrite and another the nitrite to ammonia, but others reduce direct from nitrate to ammonia.

All humus compounds and other easily oxidizable substances may actively bring about nitrate reduction, and may entirely replace bacterial nitrate reduction in peat bogs. Even when micro-organisms are present it is not always their oxygen requirement that is responsible for this reduction. Many products formed by them are easily oxidized and may bring about nitrate reduction. This is the reason why peaty, swampy, and water-logged soils are poor in nitrates. When such soils are aerated, ammonia is again nitrified.

Amino-nitrogen, Ammonium Nitrogen and Nitrate Nitrogen Assimilation.—A large number of species of bacteria and fungi have been isolated that will transform ammonia, amino-nitrogen, as well as nitrate nitrogen into protein compounds. This is a common occurrence, but it depends on various conditions.

Liberation of Nitrogen.—The liberation of nitrogen is purely chemical and may occur when amides and ammonia have an opportunity to react with nitric acid.

Denitrification.—Denitrification may be defined as the reduction of nitrates by bacteria, involving the evolution of nitrogen gas or nitrogen oxides. It should not be employed to designate losses of nitrogen gas due to the oxidation of ammonia, or the disappearance of nitrates, following their conversion into protein by micro-organisms.

There are a large number of species of bacteria, mostly anaerobic, that can reduce nitrates to nitrites and ammonia; a considerable number are known that cause complete reduction of nitrates with the evolution of nitrogen and nitrogen oxides. Denitrification occurs most often and most actively in soils containing an excess of undecomposed organic matter. They ordinarily grow under aerobic conditions, but they can also thrive under anaerobic conditions, but only when nitrites and nitrates are present. They cannot exist in the deeper strata of peat bogs.

Nitrogen Fixation by Soil Bacteria.—It is well-known that the nitrogen content in ordinary uncultivated soil rich in vegetal matter increases without human interference. This increase is due to the annexation of atmospheric nitrogen, through the agency of micro-organisms.

A number of bacteria have been isolated and grown in nitrogen-free culture solutions where they assimilated free nitrogen. Carbohydrates, such as starch, sugar and cellulose, are necessary as soil ingredients for the existence of such bacteria. Experiments have shown that as much as 53.6 gm. of nitrogen have been fixed per liter of bacterial culture solution.

Nitrogen Fixation by Nodule Bacteria.—It is common knowledge that when crops like grain and corn are raised, there is a loss of nitrogen in the soil, and that when certain other crops are raised, notably clover and alfalfa, the nitrogen content is increased. Experiments have shown

that a certain clover added more than 200 lb. of nitrogen per acre to the soil.

As is well known, the legumes in general grow a large number of nodules or tubercles on their roots and root-hairs. These nodules are filled with rod-shaped bacteria, called *bacteria adiciola.* These bacteria are capable of fixing nitrogen from the air, which becomes a part of their protoplasm; but how the clover extracts the nitrogenous substances formed is yet unexplained, but as far as known nitrogen fixation always leads to protein compounds in the plant. No other products of assimilation have ever been found.

Wood Decay

In decaying wood, the highly complex components pass into products of decreasing complexity until finally all pass into carbon dioxide (CO_2), water (H_2O), methane (CH_4), and hydrogen (H_2). Between sound wood and the final products must exist a series of intermediate products. Wood in peat, therefore, must contain many of these products in various stages of arrest.

Wood decay is accompanied by a very rapid fall in cellulose, while the lignin complex, being far more resistant than the cellulose or not attacked at all, remains almost constant. As decay progresses, there is a very decided increase in the less stable β cellulose, a large loss in the more stable α cellulose and a slight loss of the γ cellulose. The difference in sound and rotten spruce wood is shown in Table 5.[8]

TABLE 5.—*Chemical Composition of Sound and Rotted Spruce Wood*

	Sound Spruce Contained Per Cent.	Badly Rotted Spruce Contained, Per Cent.
Lignin	28.30	38.20
Cellulose, total	58.58	42.00
α Cellulose	63.35	17.00
β Cellulose	10.37	74.60
γ Cellulose	28.08	8.40
Pentosan	11.88	8.50
Methylpentosan	1.88	2.84
Ash	0.17	0.46
Cold water soluble	2.30	6.58
Hot water soluble	3.90	11.92
1 per cent. NaOH soluble	8.83	44.00
7.14 per cent. NaOH soluble	18.80	62.36
Ether soluble	1.24	1.47

[8] M. W. Bray and Joseph Staidl: The Chemical Changes Involved during Infection and Decay of Wood and Wood Pulp. *Ind. & Eng. Chem.* (1922) **14**, 35.

In Table 6, the differences in sound heartwood, partly rotten heartwood and more completely rotted heartwood of the Douglas fir is given:[9]

TABLE 6.—*Composition of Decayed Wood*

	Sound Wood, Per Cent.	Partly Rotten Wood, Per Cent.	More Completely Rotted, Per Cent.
Cold water soluble	4.03	1.76	1.16
Hot water soluble	2.23	4.19	7.77
Alkali soluble	10.61	38.10	65.31
Cellulose	58.96	41.66	8.47
Acid hydrolysis	0.71	0.28	0.17
Pentosan	7.16	6.79	2.96
Methylpentosan	2.64	3.56	6.05
Methoxyl group	3.94	5.16	7.80
Moisture	9.81	10.63	9.09
Ether extract	2.71	2.05	2.72
Ash	0.15	0.15	0.65

As decay proceeds the cellulose disappears more and more, leaving finally very little or nothing but the so-called humin, a product of the original lignin of the lignocellulose proper. Recent experiments with fir wood containing 60 per cent. cellulose, after 6 months rotting contained 26.8 per cent., after 1 year 10.90 per cent. and after 3 years 6.05 per cent. The lignin complex lost about 3 per cent. in 3 years and then remained constant. It must be remembered, however, that wood contains a number of adventitious substances, like fat and waxes and others. These are not decomposed by organisms of decay, as shown in the ether extracts.

The foregoing account and tables are from studies made on materials that were infected with mixtures of organisms. Bray and Andrews[10] later carried on investigations at the Forest Products Laboratory, Madison, Wis., to show the chemical changes brought about in wood when infected by specific organisms in pure culture. The results are shown in Table 7.

[9] Robert Evstafieff Rose and Martin William Lissi: The Chemistry of Wood Decay. *Ind. & Eng. Chem.* (1917) **9**, 284.

[10] M. W. Bray and T. M. Andrews: Chemical Changes of Ground Wood during Decay. *Ind. & Eng. Chem.* (1924) **16**, 137.

TABLE 7.—*Analysis of Ground Wood Based on Equal Weights of Sample Analyzed (Per Cent.) (after Bray and Andrews)*

Sample	Organism or Culture No.	Storage Time, Months	Water Soluble		1 Per Cent. Alkali Soluble	Lignin	Cellulose	α Cellulose	β Cellulose	γ Cellulose	Pentosan	Methoxyl	Copper No.	Ash
			Cold	Hot										
2544	Sound	0	0.0	1.2	10.1	29.7	60.0	60.5	24.5	15.0	12.0	5.5	4.4	0.6
100	4620-2	6	11.1	17.95	54.9	38.0	36.7	19.6	67.2	13.2				
102	4620-2	12	14.8	22.2	66.8	53.4	21.8							5.75
182	4620-2	36		16.5	70.0	71.0	16.1				6.8	7.2	23.0	
130	Fomes roseus	6	3.2	6.4	33.0	34.1	49.4	49.7	38.9	11.5				
131	Fomes roseus	9	3.7	5.6	33.6	34.8	50.7							
157	Lentinus lepideus	6	9.6	15.1	52.3	36.7	40.9	51.7	36.8	11.5				
158	Lentinus lepideus	9	13.9	22.6	58.2	41.1	37.1							
106	4620-1	6	12.3	17.7	52.4	39.5	37.3	23.6	68.4	8.0				
107	4620-1	9	16.6	22.8	62.2	43.1	27.2							
108	4620-1	2	14.9	21.2	62.0	46.5	27.6							
148	Peniophora tabacina	6	5.6	10.4	40.4	32.1	46.8	55.4	34.2	10.4				

Table 7 shows only the amount of the constituents of decayed wood in percentages of the decayed wood itself; Table 8 shows the percentage of the different constituents based on the original dry wood:

TABLE 8.—*Analysis of Ground Wood Based on Equal Weights of Original Sample (Per Cent.) (after Bray and Andrews)*

Sample	Organism or Culture No.	Storage Time, Months	Loss Due to Decay	Water Soluble		1 Per Cent. Alkali Soluble	Lignin	Cellulose	α Cellulose	β Cellulose	γ Cellulose	Pentosan	Methoxyl	Copper No.
				Cold	Hot									
2544	Sound	0	0.0	0.0	1.2	10.1	29.7	60.0	36.3	14.7	9.0	12.0	5.5	4.4
100	4620-2	6	27.12	8.1	13.1	40.0	27.7	26.8	5.1	18.0	3.5			
102	4620-2	12	49.5	7.5	11.1	33.4	26.7	10.9						
182	4620-2	36	62.4		6.2	26.3	26.7	6.05				2.56	2.7	8.65
130	Fomes roseus	6	10.3	2.9	5.7	29.6	30.6	44.3	22.0	17.2	5.1			
131	Fomes roseus	9	12.94	3.2	4.9	29.2	30.3	43.8						
157	Lentinus lepideus	6	21.54	7.5	11.8	41.0	28.8	32.1	16.5	12.0	3.5			
158	Lentinus lepideus	9	30.31	9.7	15.7	40.6	28.6	25.8						
106	4620-1	6	22.2	10.8	13.7	40.8	30.7	29.0	6.9	19.8	2.3			
107	4620-1	9	33.11	11.1	15.3	41.6	28.8	18.2						
108	4620-1	2	38.63	9.3	13.0	38.0	28.5	16.9						
148	Peniophora tabacina	6	13.5	4.8	9.0	34.9	27.7	40.5	22.5	13.9	4.2			

Remaining Residue of Wood or Humus Formation

During the process of decay, lignin does not decay uniformly and probably proceeds very slowly by stages. Few experiments have been carried on and little has been recorded that furnishes any knowledge of the lignin degradation or so-called humus formation.

In consideration of the facts known concerning lignin, lignocellulose and cellulose, it may be assumed that the residue of thoroughly decayed

wood is the same as the lignin prepared from wood by artificial means. This reasoning has not been verified by exact chemical means; on the other hand, however, nothing has been furnished to show the contrary.

Bray and Andrews found that when in decaying wood the results were calculated on the original sound-wood basis, the value of the lignin remained practically constant or only a slight decrease may be observed. After one year of storage after inoculation of lignin, a 3 per cent. loss was observed; after three years of storage no further loss resulted. This loss is accounted for by the loss of the methoxyl group, which in this particular case was 2.8 per cent. of the original wood.

How long the lignin will resist the attack of micro-organisms under favorable conditions is not known. According to certain observations so-called rotten wood and rotten logs in the primeval forests must have been exposed in this condition for several hundred years, yet are still fairly compact. The same forests show that the tree trunks finally do disintegrate to such an extent that the remainder is merely in the form of a dust. How much older these are, it is not possible to estimate. In the peat bog, further decay is checked relatively early.

Thoroughly rotted wood consists partly of water-soluble substance, partly of alkaline soluble substances, and an insoluble residue much richer in carbon. A reliable record has been made by Wehmer.[11] He separated rotten fir wood, Picea exelsa, into the following substances:

Humin I. Cold-water soluble. A brown-black, glistening, hard lac easily soluble in water, extractable with hot water.

Humin II. Hot-water soluble. A coal-like, dull powder, composed of small spherical grains of 1–5 mm. in diameter, extractable with hot water, precipitating on cooling as a brownish gray sediment.

Humin III. Alkali (2 per cent.) soluble. Glistening, brownish black, brittle pieces, unsoluble in water, extractable with 2 per cent. solution of soda as a dark brown solution, coagulating with acids in fluffy flakes.

Humin IV. An insoluble peat-like compact brown residue retaining the woody structure. Table 9 shows the percentage composition:

TABLE 9.—*Composition of Substances in Rotten Fir Wood*

Substance	C, Per Cent.	H_2, Per Cent.	O_2, Per Cent.	Per Cent.
Humin I	46.4	6.0	47.5	12.5
Humin II	51.6	5.6	42.8	1.5
Humin III	64.1	8.0	28.0	7.4
Residue	60.5	9.35	30.14	51.6
Water				27.0

[11] Zum Abbau der Holzsubstanz durch Pilze. *Ber.-Deutsh. Chem. Gesel.* (1915) **48,** 130–134. *Rev. Koll Ztschr.* (1915) **16,** 181.

A sample of wood, with a 51 per cent. carbon content, during complete decay yielded (1) 50 per cent. of CO_2, H_2O, and some fungal remains; and (2) 50 per cent. of humified wood, with a carbon content of 56.8 per cent. The humified wood was separable into (*a*) 15 per cent. water-soluble substance with a carbon content of 46.4 to 51.6 per cent., (*b*) 35 per cent. alkali-soluble substance, with a carbon content of 64 per cent., and (*c*) 50 per cent. insoluble substance, with a well-preserved woody structure with traces of cellulose.

Pectin.—Pectin is readily decomposed by micro-organisms. An enzyme, pectinase, first hydrolyses it to arabinose. This sugar is then fermented through the agency of zymase, resulting in some cases in carbon dioxide and butyric acid, and in alcohol, formic acid, acetic acid and acetone in other cases. A number of bacteria have been isolated that will decompose pectin but no other compound of the plant. A number of fungi will also dissolve pectin.

The cells of all plant tissues are cemented together by means of a thin layer of pectin, called the middle lamellæ. On hydrolysis of the middle lamellæ, the tissues disintegrate into their fibers or cells; fruits in such cases are said to become mushy. The retting of hemp and flax depends on the solution of the middle lamellæ by means of bacteria.

Hemi-cellulose.—The hemi-celluloses, such as pentosans, mannans, and xylans, are also dissolved by a series of bacteria. The hydrolyzing enzyme is xymase. No bacteria has been isolated that will decompose galactan.

How Plants Contribute to the Bog

During every growing season plants grow new leaves, young shoots, flowers, seeds, pollens, and spores; wood and bark are added to the stems, besides, certain secretions such as gums, resins and tannins, mostly products of disassimilation, are deposited in ducts and reservoirs throughout the plants. Also, every year the plants shed the leaves, blossoms, pollens, spores, part of the bark as a natural sequence of the life processes of the plant; twigs, branches, and trees are broken or torn down by the wind, ice, sleet, and snow. Trees or parts of trees die through injury and sooner or later drop in a semi-decayed condition. Many trees, on account of the loose ground they live on, are not able to hold up and gradually lean over more and more until they lie flat on the ground, and sooner or later are buried dead or alive by subsequent debris. Thus, in the long run, an equilibrium is maintained between growth and drop.

The dead material, as long as uncovered by water, undergoes a rapid decay, begun by fungi and maintained by fungi and bacteria. Fungi soon transform these plant parts into a soggy mass and prepare it for the attack of bacteria. As long as it remains exposed to the air, decay proceeds rapidly. Much of it decomposes completely, some of it remains

in a semi-decayed condition. In this state, much of it crumbles and much of this is transformed into a fine debris. In this condition, the mass is sooner or later covered by subsequent decaying vegetable matter and becomes submerged below the water level. Once in this position, decay proceeds through bacteria alone and very slowly, partly on account of the exclusion of air and partly on account of the antiseptic condition of the mass caused by the decomposition products themselves. Slow changes, however, are taking place in the bog, and even at considerable depths below the surface. This is shown by the change from a more immature peat in the upper strata to more and more mature peat in the deeper strata. Living bacteria are found at all depths of the bogs, and gases, mostly methane, are constantly being given off from the deposit. These bacterial activities deprive the deposit more and more of its oxygen and render it a highly reducing agent.

Differential Rates of Decomposition of Plant Substances

Not all plant substances decompose with the same ease, in fact some do not appear to be attacked at all by agencies of decay while others rot very quickly. The plant components that constitute the living part of the plant, as also the plant foods and reserve substances such as the sugars, starches, and gums, are relatively easily decomposed, and relatively little remains of them during ordinary rotting on the surface. The cell-wall components, also, vary greatly in the ease with which they rot or decompose. The hemi-celluloses, hexoses and pectins, decompose more easily than the celluloses, which are quite resistant. The cuto-celluloses are the most resistant to decay. The largest part, as has already been intimated, is contributed by the wood of plants.

As shown, in rotting wood the cellulose disappears rapidly, while the lignin complex or certain parts of the lignone complex remains; and it is this part that mainly contributes to peat. From laboratory experiments, it would seem that after three years of exposure in moist conditions no (or but little) cellulose remains.

Those substances that are here called the "protective substances," are all resistant to agencies of decay. To them belong cuto-cellulose, wax, fats of higher molecular weight, and resins. The cuticles of many plants, the spore exines and pollen exines, are largely composed of such substances and undergo but little chemical change. The waste products, in general disassimilation products no longer available as foods, are also not readily decomposed; to these belong the resins, terpins, alkaloids and purine bases. Because these substances undergo little or no decomposition and as those substances that form the bulk of the plant mass undergo considerable decomposition, the former substances remain in relatively very much larger percentages than found in the plant originally. It is thus seen that a selection or an accumulation of the more

resistant substance is going on all the time and the more resistant the less is their loss, and that the more and most resistant substances accumulate proportionately faster than the least and the less resistant. It is another case of the survival of the fittest.

Differential Decay of Different Species

It is well known that certain species of plants are subject to decay much more readily than others. Among the swamp-loving plants, it may be observed that a black ash is decomposed more readily than a spruce or a balsam, a balsam quicker than a tamarack, and a tamarack quicker than a cedar. The black ash is the least resistant and the cedar the more resistant tree to biochemical decay. In the same swamp, a black ash may be decomposed to a debris, while a cedar tree lying beneath it is still hard and sound.

If the different peat-forming trees always grew in a mixed condition, a differential decay would not visibly influence to produce different kinds of peat. But we do not find them growing that way. It may be observed that, because of certain conditions, the kinds of plants growing in a swamp are restricted to one or two species with only a few other species sparingly intermixed. We thus come to speak of a cedar swamp in which by far the most predominant tree is the white cedar, with only a few other species intermixed. Likewise are the tamarack swamps, the black-ash swamps, the bald cypress swamp, the spruce swamp and so forth.

When the peat deposits formed by these different floras are examined, it is found that each has characteristics of its own. The black ash, which is quickly attacked, furnishes a much macerated peat deposit; on the other hand the white cedars furnish a deposit characterized by a large number of tree stems; and tamaracks furnish a well-macerated peat but characterized by its resinous matter.

The foliage of the trees that form the flora of a swamp influence the nature of the deposit as much or more than the nature of the woody parts. The surface layer of a cedar swamp differs widely from that of a tamarack swamp or a black-ash swamp as a result of the difference in the decomposibility of the leaves, and surely the peat derived from them must differ as much.

The exact cause of the difference in durability in wood is not known, but it is quite certain that the chemical composition of the wood is a large factor. It has been shown by Hawley, Fleck, and Richards[12] that woods in which the extracts are the most toxic are also the most resistant to decay. It was also found that the extract of the heartwood

[12] L. F. Hawley, L. C. Fleck, and C. A. Richards: The Relation between Durability and Chemical Composition in Wood. *Ind. & Eng. Chem.* (1924) **16**, 699.

is more toxic than that of the sapwood. It has always been supposed that the lesser durability of the sapwood was due to the larger amount of sugars and starch in it, and thus further the growth of micro-organisms. Although this may be a factor, the greater toxic content of the heartwood is probably the greater.

Plant Matters Buried Alive

It has been mentioned that a considerable number of trees recline more and more until they lie flat on the ground and eventually are buried alive. Secondly the root complex of the flora of the swamp, while they never penetrate far into the peat stratum below, living roots remaining relatively near the surface, by the time they die are covered by a considerable amount of debris. Such plant matter evidently does not go through the same phases of decay as those that decay on the surface with complete access of air. Such plant parts, in the first place, will not be macerated, but will be transformed whole. Whether the changes brought about in them through decay in a buried condition differs from that of decay in the air remains to be seen. Decay under such conditions is probably extremely slow. Fungi are excluded at all times and reasoning from the chemistry of wood decay, cellulose fermenting bacteria only can be active, living under strong reducing conditions, fresh peat being a strong reducing agent. We may have here a solution of the origin of mineral charcoal.

Variations in the Degree of Decay and Maceration through Varying Conditions

If the conditions of water level and moisture in a certain bog were constant throughout its life, the deposit would be uniform in texture, structure, and composition. In a large number of deposits, the natural sequence in the life of a deposit is from an aquatic bog to the woody swamp. To reach the last stage, it has to go through the marsh stage, the sedge stage, the shrub stage, the mixed shrub and tree stage, and finally reaches the permanent tree stage. In sounding such a deposit, each stage is recognizable by the specific kind of peat that was deposited. A number of such deposits are found in the peat regions of Michigan and Wisconsin. Provided that no other cause appears, these bogs pass from an aquatic condition, through the various stages of diminishing moisture until the mesophytic stage is reached, where it will remain. The climax is reached simply by filling up the depression with the debris of its own vegetation. Other causes may modify the conditions. Natural erosion may remove a barrier and thus aid in the drainage, or the earth's surface, including the swamp, may rise gradually changing drainage conditions, or even removing the deposit already established. Artificial drainage is the most common cause today in reversing swamp conditions. In parts

of Wisconsin and Michigan, where the earlier settlers found impenetrable peat bogs, today are found wheat fields, celery fields, and orchards. Ten years ago, Sheboygan Marsh in Wisconsin was an impenetrable peat bog, with a peat deposit about 10 ft. deep; in another ten years, between 6000 and 7000 acres will be transformed into truck fields and orchards.

The opposite transition may also take place. A swamp may begin with the mesophytic wooded stage, and gradually be transformed into the aquatic stage, passing through the same phases as the aquatic to wooden swamp series, in the reverse order, increasing in moisture until finally a typical aquatic stage is reached and finally may be covered up by inflowing mud and sand. This state of affairs may be brought about by a subsiding area of the earth's crust. A good example of this condition is found in the Dismal Swamp of Virginia and North Carolina, with Lake Drumond in its midst, in which the stumps and a few remaining trees bear mute witness of a once woody swamp. In this case, also, each successive stage deposited its characteristic kind of peat, similar to that of the aquatic to mesophytic series; the transitions of course may be gradual and almost imperceptible. In the coal measures, similar transitions are recorded in the earth's strata, as will be noted further on.

Composition of the Peat Bog

From what has been said, it should not be difficult to get a fair idea of the composition of peat in all its varieties. In a discussion of peat, it is essential to take into consideration the different kinds of peat formed under different conditions, as each type of bog gives rise to its characteristic kind of peat. For example, the open-water bog gives rise to a much macerated, mucky peat, the sapropel of Potonie; the marsh furnishes a peat often alluded to as "lebertorf;" and the tree-covered swamp (Fig. 1) gives rise to the woody peat. These three kinds are set off arbitrarily as types; several other types and every possible intergradation may exist.

The Open-water Deposit

The deposit formed in the open-water bog consists of a slimy ooze, composed largely of the most resistant plant products of plants that lived in and around the bog. Among these are the cutinized coverings of stems and leaves, the waxy and oily content of stems and leaves; seeds and seed coats, pollens and spores. Pollens may be blown in from flora surrounding the bog. Humic or woody plant degradation matters are always present in relatively small, but in greatly varying, proportions. Algal matters do not contribute any appreciable part. Deposits of this kind approach in composition the cannel coals of the older periods.

Fig. 1.—Close-up view of peat bog of Wisconsin; foreground is under water; partly covered tree trunks are shown; hummocks indicate buried tree trunks; peat is approximately 8 ft. deep.

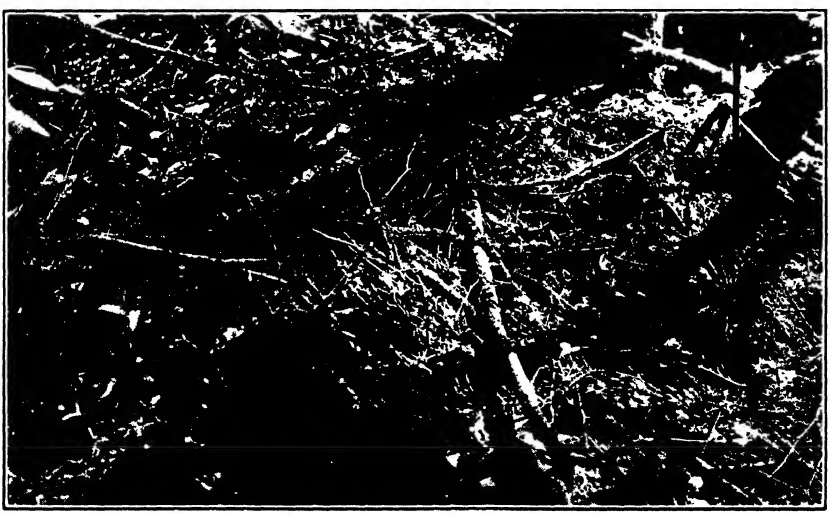


Fig. 2.—Close-up view of surface of same peat bog, showing nature of litter on surface; foreground is partly under water.

FIG. 3.—LUMP OF AIR-DRIED PEAT, FROM BOG SHOWN IN FIG. 1, SHOWING A LARGE NUMBER OF SMALLER FRAGMENTS OF WOODY PEAT, SOME MICROSCOPIC IN SIZE, EMBEDDED IN THE ATTRITUS. NATURAL SIZE.

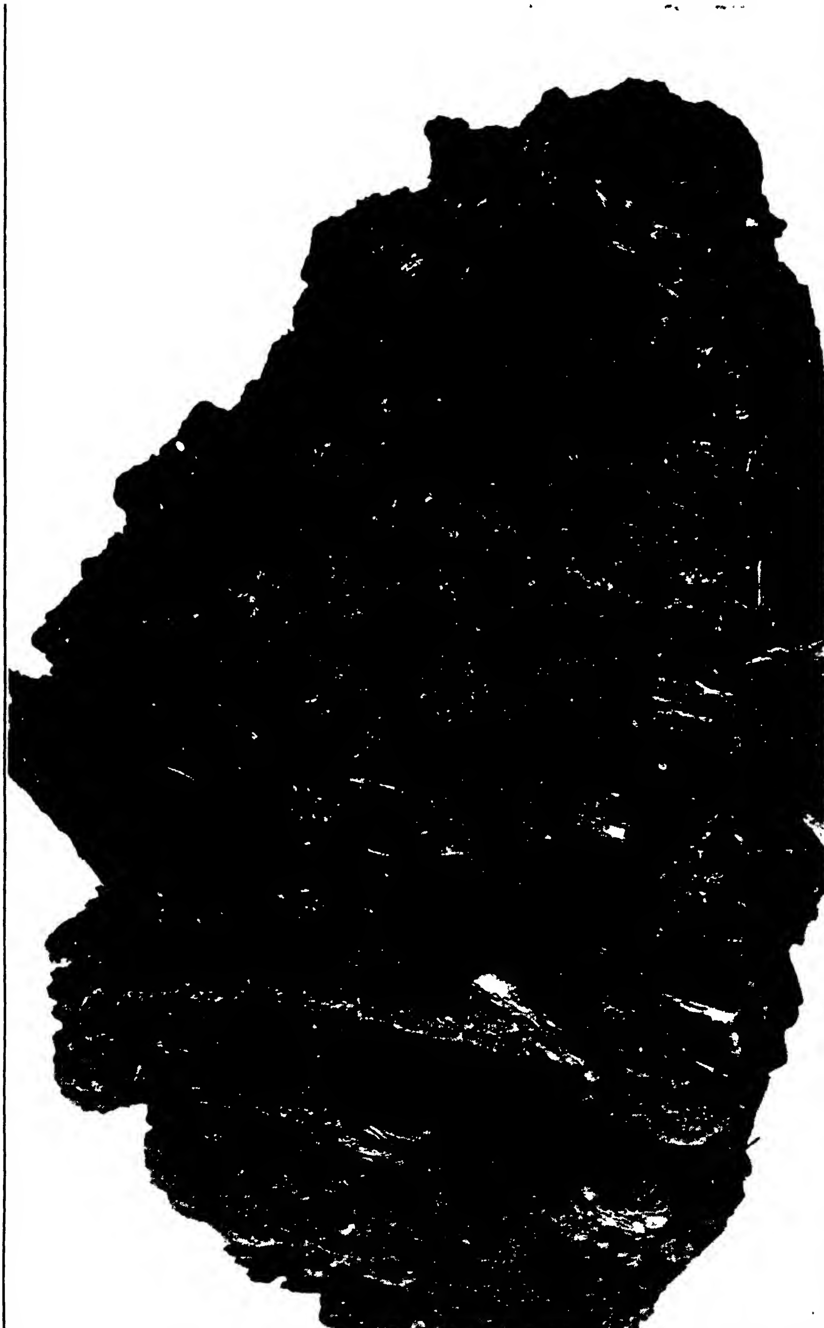


FIG. 4.—LUMP OF AIR-DRIED PEAT, FROM BOG SHOWN IN FIG. 1, CONSISTING LARGELY OF ATTRITUS, CONTAINING A LARGE NUMBER OF SMALL FRAGMENTS OF WOODY PEAT. NATURAL SIZE.

The Marsh Peat

The product of the marsh is composed essentially of the same constituents, except that it contains a much larger relative amount of humic matter, and occasionally small fragments of woody matter, fragments of the haulms of sedges, grasses, and seeds. Mosses and lichens may have been prominent contributors.

The peat of this type of bog may be subdivided into various kinds, according to the predominant class of plants contributing. The mosses, particularly sphagum, may have been the chief contributors; or grasses, or sedges, or both grasses and sedges may have been the main contributors.

Peat of the Wooded Swamp

Peat formed by the wooded-swamp type (Fig. 1) is in every respect analogous to an ordinary lignite, subbituminous or bituminous coal. This kind of peat is, therefore, of greatest interest. The more mature peat begins a foot or so beneath the surface layer, and usually extends to within a short distance from the bottom or may extend to the bottom. This mass consists of the same components as the surface layer, only in a much further advanced stage of decay. Logs or parts of tree trunks, fragments of these and larger parts of branches and roots constitute the more bulky components. Between these are lodged smaller fragments of these same constituents (Fig. 3); all is embedded in what appears like a dark-brown to black mud. This is the attritus; see Figs. 3 and 4.

Matter derived from the woody parts of plants forms by far the largest portion of the ordinary woody peat. It consists of what is ordinarily termed rotten wood. We are today much better informed as to the nature of rotten wood than we were a few years ago.

Chemical Nature of Peat Wood

Laboratory experiments have shown that when wood is inoculated with wood-destroying fungi, only a small percentage of the cellulose of the wood remains after three years, but the lignin of the wood remains nearly constant. If wood is exposed under favorable natural conditions, it becomes the host of a number of different fungi as well as bacteria, and decay proceeds more rapidly. The time of exposure of the plant matter of the swamp of both fungi and bacteria in the air is on the whole much longer than three years. It may be assumed, therefore, that the decay of the wood above the surface is quite complete. After the decaying wood is submerged, if any cellulose has escaped destruction, bacteria still continue their activities. It must be remembered that a considerable number of trees recline more and more until they finally lie flat on the ground, still alive, and are gradually covered up alive. These will

never be attacked by fungi, and bacteria alone can act on them. Similarly, the greater proportion of the roots of the swamp flora, although always relatively close to the surface, are buried under a considerable quantity of debris or are even submerged beneath the water and are not subjected to aerial decay but to bacterial decay only. How readily these constituents are attacked and how far the cellulose is destroyed in them remains to be seen. In sounding a bog from top to bottom, it is found that the upper strata still contain some cellulose, but this decreases in amount downward, and in the deeper strata is but sparingly found if at all.

It has always been a question as to what had become of the cellulose. Although cellulose as such could not be found, or but sparingly, in peat wood, could it not have been changed into some residual substance, and if so what was its nature? It is now known that the first decomposition of cellulose is by hydrolysis, and that its first decomposition product is cellobiose, which splits into glucose. Being a good food substance glucose is easily fermented to simpler products. It is also known that the lignin of wood is not decomposed easily either by means of organic enzymes or by chemical reagents, except that it may lose its methoxyl groups. Although it is not known what becomes of the lignin in the end under moist aerial conditions, it is known that enough of it, in fact by far the most of it, escapes decomposition and is finally submerged, where it apparently does not decompose much further. If any further decomposition takes place, we are not as well informed as in the case of cellulose (Figs. 7 and 8).

The hemi-celluloses, pentosans and xylans, starches and gums have also disappeared. The middle lamellæ in many cases are still recognizable, in some cases none is visible.

Laboratory experiments also show that the waxes, oils, and resins are not destroyed by micro-organisms; tests on peat bear out this statement. What part of these remain in the wood in natural conditions is not well known. All that is known is that such woods yield certain amounts of soluble substances.

When examined microscopically, thin sections of thoroughly rotted peat wood reveal much foreign matter in the fibers (Fig. 9). Some of these may be identified as gums, waxes, resins, and oils. No exact account has been taken, and all that can be said is that a considerable quantity of foreign matter is commonly found in the cells and fibers of various wood tissues after decay.

Physical Nature of Peat Wood

Mature peat wood is partly soluble in hot water and almost completely soluble in a weak solution of potassium or sodium hydroxide. This yields a dark brown, in dilute solutions, to black, in more concen-

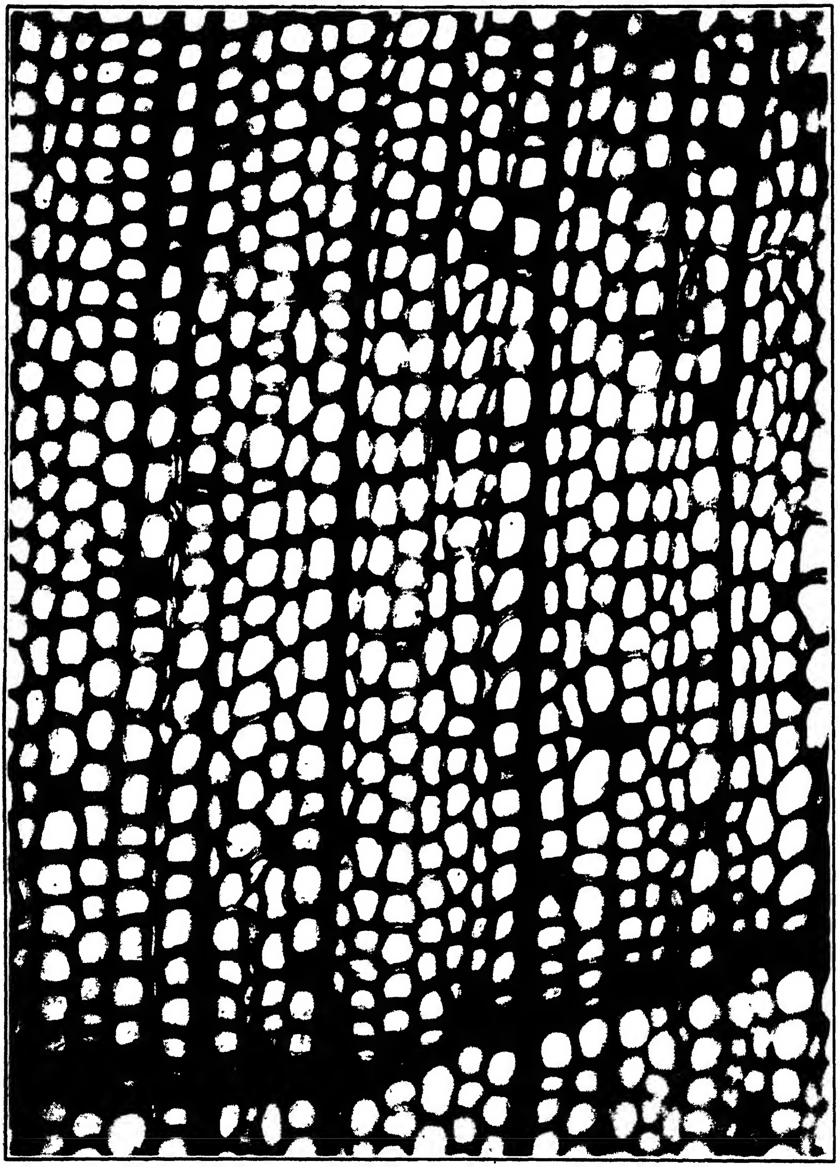


FIG. 5.—THIN CROSS-SECTION OF SOUND WOOD OF CONIFER, *Podocarpus Chiliensis;* RAY CELLS AND RESIN DUCTS CONTAIN RESIN. × 200.

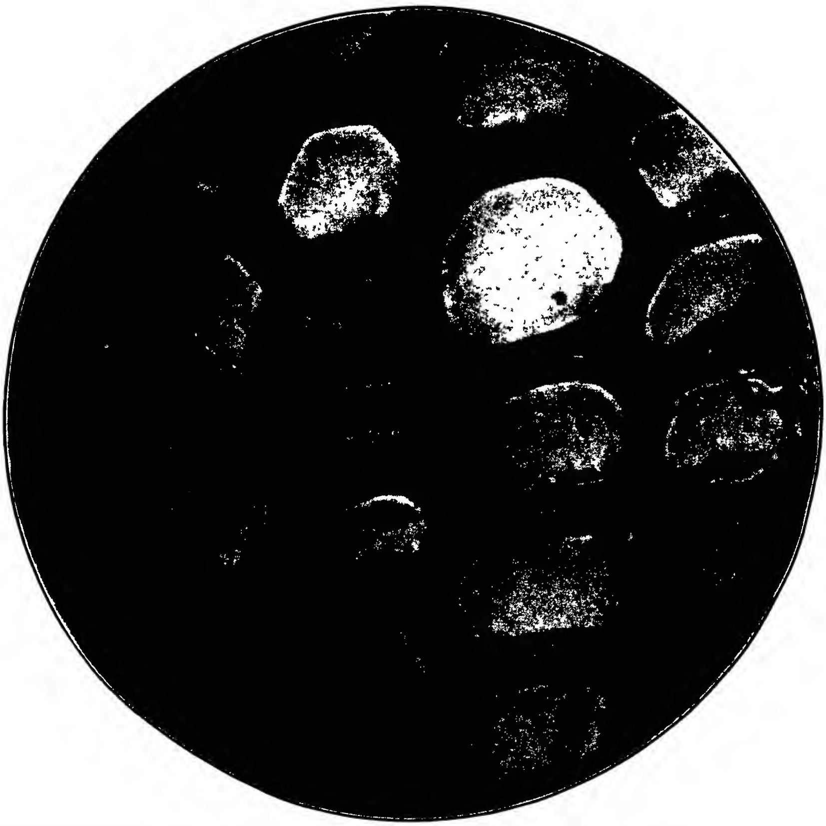


Fig. 6.—Part of thin cross-section of conifer shown in Fig. 5; cell walls are compact and well layered; middle lemellum is clearly shown. × 1000.

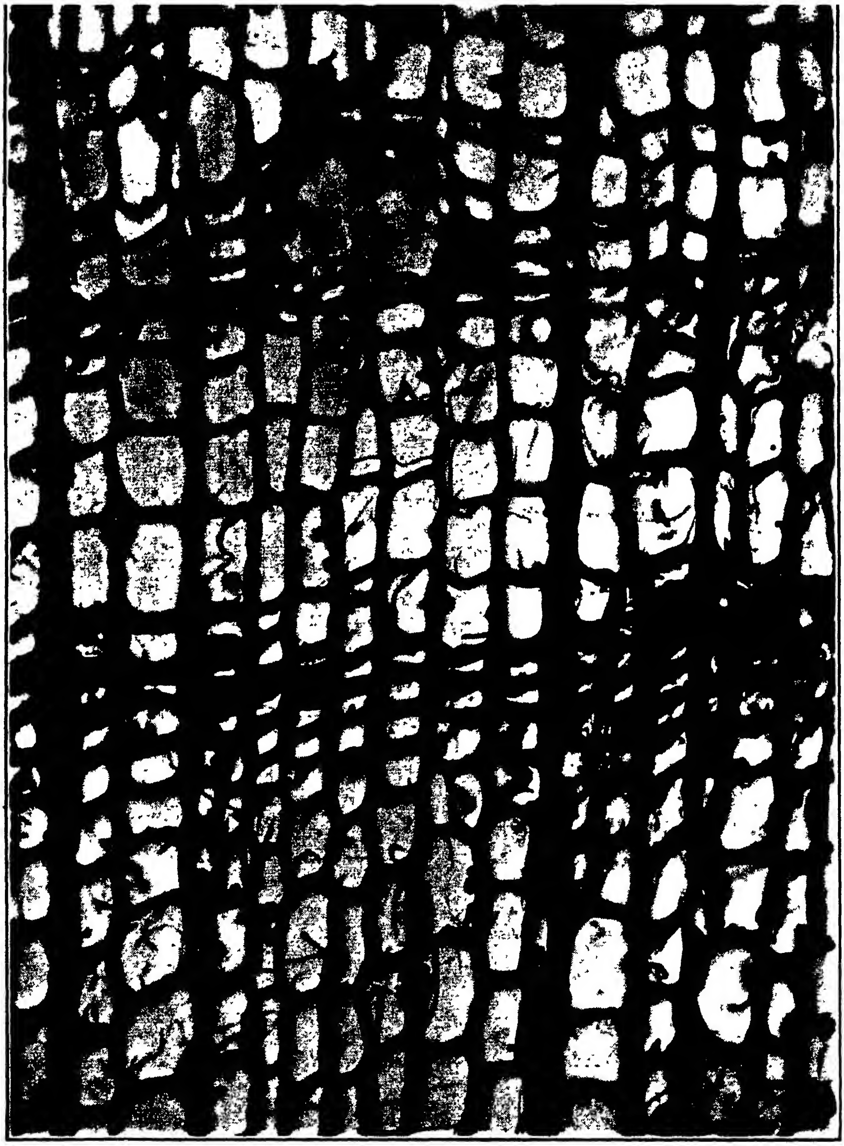


FIG. 7.—THIN CROSS-SECTION OF FRAGMENT OF PEAT WOOD, SUCH AS IS SHOWN IN FIG. 3; COMPARE WITH FIG. 5; CELL WALLS ARE RAGGED AND TATTERED AND HAVE LOST THEIR EVEN FORM; HYPHÆ OF FUNGI ARE SHOWN. × 200.

FIG. 8.—PART OF THIN SECTION OF WOODY PEAT SHOWN IN FIG. 7; SHOWS CELL WALLS OF ROTTEN WOOD IN DETAIL AND HYPHÆ OF FUNGI; NOTE SHREDDED APPEARANCE; ONLY MINUTE QUANTITIES OF CELLULOSE HAVE REMAINED. × 1000.

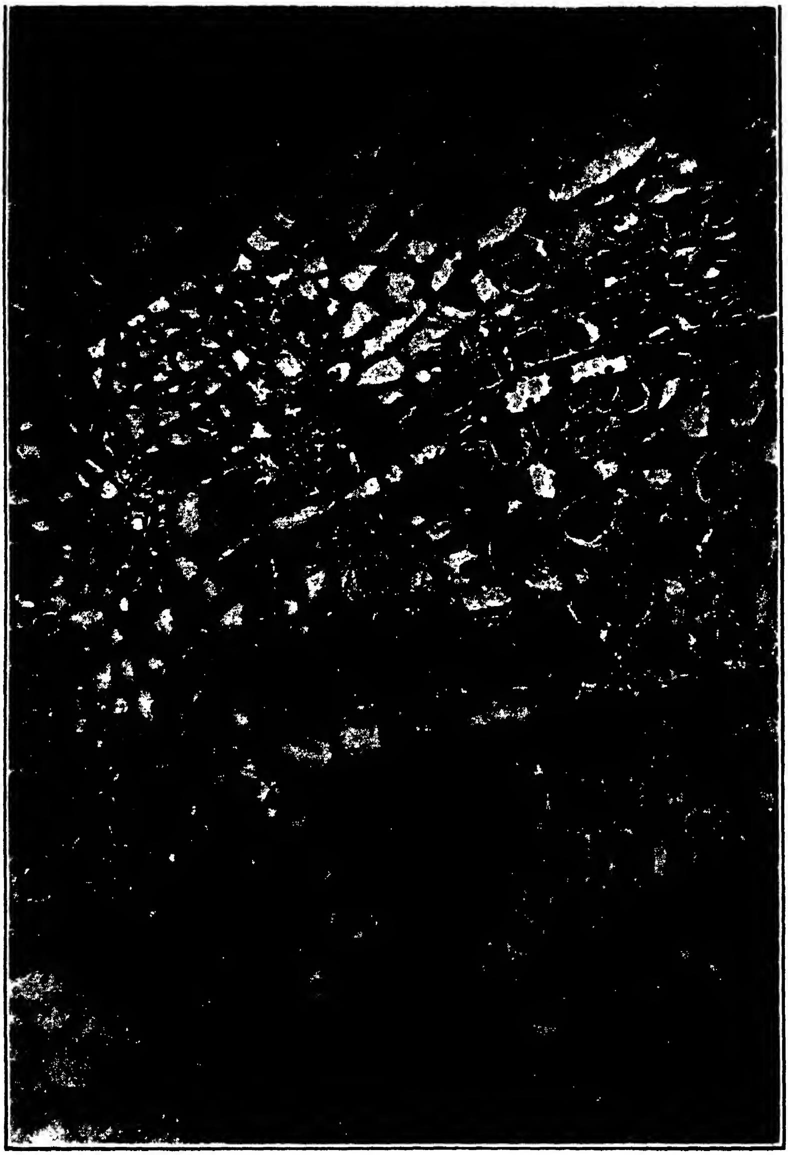


FIG. 9.—THIN CROSS-SECTION OF FRAGMENT OF PEAT WOOD, SUCH AS IS SHOWN IN FIGS. 3 AND 4. THIS PIECE OF ROTTEN WOOD CONTAINS CONSIDERABLE NON-RESINOUS CELL INCLUSIONS; CELL WALLS ARE IN AN ADVANCED STATE OF DECAY AND CELLULOSE HAS ALMOST COMPLETELY DISAPPEARED. $\times$ 200.

FIG. 10.—THIN SECTION OF CARBONIZED ATTRITIOUS PEAT; HORIZONTAL STRIÆ REPRESENT CUTICLES; ATTRITUS IS COMPOSED LARGELY OF CUTICULAR DEGRADATION MATTER, DEGRADATION MATTER OF LEAF TISSUES, SOME WOODY MATTER, SPORE AND POLLEN MATTER, AND SOME RESINOUS MATTER. × 200.

trated solutions, which precipitates on addition of acids. This substance is commonly called humin, humic acid, ulmin and ulmic acid.

Peat wood no matter how large the fragment may be, has retained its normal cell structure at the time when taken from the bog; the cells are in the natural position and, to a large extent, hold their natural shape. When seen under the microscope, in thin section, the thickness of the cell walls does not seem to have diminished appreciably as compared with sound wood of the same species. The matter composing the cell walls, however, differs much in appearance from that of sound wood. It is loose and granular in structure, although it has retained some of its layering. The middle lamellum is usually present, but may have separated from the main wall (Figs. 7, 8, and 9).

Mature peat wood, when fresh from the bog, is soft and friable, may easily be cut with the spade, is pliable, and fairly plastic, almost like clay.

Under the ultra-microscope, the cell walls are shown to be typical gels. When dried, peat wood hardens into the consistence of hard rubber or bone, and its volume shrinks considerably. When now examined under the microscope, the cell walls have largely collapsed and appear much thinner than when examined wet and fresh from the bog. The mass of mature peat wood has all the characteristics of a hydrogel. This is an important characteristic in consideration of the future coalification. All hydrogels, when dried, change into a hard, brittle, almost glassy, substance; its quality is dependent on its purity.

Attritus

The attritus is the finely divided solid residue of decay and consists largely of parts of plants that resisted complete decay or were not attacked at all. It contains, therefore, a large proportion of the more resistant plant products rather than of the less resistant. It is composed of the degradation matter of anything and everything that grew in the bog, and consists therefore of a large variety of substances (Fig. 4). To the naked eye, the attritus appears as a black mud, or as a black jelly-like substance; and when rubbed between the fingers has a jelly-like, slimy feel. When observed under the microscope, however, it is shown to consist of definite and specifically recognizable particles; consisting of bits of plant parts, isolated cells or part of cells, bits of tissues of wood, leaves, bark, roots, bits of tissue of mosses and lichens, fragmentary cuticles, pollens, spores and resinous particles, and some dirt (Fig. 10). These different components vary considerably in proportion from one swamp to the other and from one horizon of the same swamp to another.

The humic matter of the attritus may be derived from the wood, bark, pith, leaves, mosses, lichens, gums, starch pectins, and other carbohydrates. It is thus seen to be of a varied origin. It is largely present as definite particles and but a very small part of it is colloidally dispersed.

Much of it can, however, be dispersed colloidally by means of certain reagents.

Cuticles of leaves and stems are always present and are easily recognizable (Fig. 10). They are in the form of smaller or larger fragments and often are finely macerated. This constituent cannot be dispersed colloidally nor is it soluble in ordinary solvents. Spores and pollens also are always present and easily recognizable. This constituent also cannot be dispersed colloidally nor is it soluble.

Resinous matter also is always present in various forms and is easily recognizable. Resinous particles are liberated from rotted and disintegrated wood, bark, and leaves. Like the cuticles, pollens, and spores, resinous matters are not subject to decay, and hence remain constant as based on the original material, and have been concentrated when based on the amount of its residual matter. Resins are soluble by means of various organic solvents, but cannot be easily dispersed colloidally.

Waxes and fats or oils are present but cannot be distinguished readily microscopically, yet they can be extracted by means of various solvents. Besides these constituents, theoretically considered, a considerable number of other plant products must be present, either as original compounds or degradation products, such as of tannins, alkaloids, glucosides, and the purine bases. But they cannot be observed by ordinary microscopic means, and little is known about them in peat. But that plants have contributed these to the coal is clearly shown by the presence of certain decomposition products of coals.

THE MICROSCOPIC CONSTITUTION OF COALS OF DIFFERENT RANKS AND AGES

Coalification Processes

The transformation of the plant substances into peat was largely brought about by fungal and bacterial agencies. The sum of the processes have been called biochemical. As the peat bog was gradually covered up by clays, sand, and silt, the biochemical processes gradually ceased, but the relative increment of the carbon content and the relative decrease in oxygen content begun by the biological agencies continued.

How much longer the biological activities continued after being covered is not known and is an important problem for consideration both as to how long bacteria survive and how long the enzymes secreted by them remain active after their death. Bacteria have been found at all depths (up to 30 ft.) of recent peat bogs. To deposit this amount of peat must have consumed hundreds of years. If bacteria can survive under such conditions at such length of time, the question normally arises when do they cease to exist and what destroys them? It is also well known that enzymes will remain active under favorable conditions for a considerable period after the death of the organisms giving rise to them. It would,

therefore, also be of considerable interest to know how long the enzymes remain active in the bog after the death of the bacteria themselves.

The further changes brought about in the peat substance after being covered and which continue through the whole series of the coals from peat to anthracite have for short been called "coalification." In recent years, the processes involved have been termed "dynamochemical," in contradistinction to the biochemical. To show graphically something of the nature of the changes, the ultimate analyses of types of coals in each stage of the series from peat to anthracite are given in Table 10. To this is added that of wood and lignin for comparison.

TABLE 10.—*Analyses of Coals by Stages of the Coalification Process*

Substance	C, Per Cent.	H_2, Per Cent.	O_2, Per Cent.	N_2, Per Cent.
Wood	50	6.0	43	
Lignin (Schwalbe)	55.6	5.8	38.4	
Lignin (König)	64.85	4.86		
Lignin (Klason)	66.67	5.49		
Lignin (Fischer & Schrader)	64.70	5.68		
Peat, wooded, Wisconsin	58.88	5.00	33.10	2 58
Brown coal, Saxony	64 4	6.6	29.0	
Coal, carboniferous lignites, Moscow, Russia	70.0	6.3	20.9	2.10
Lignite, Burlington, North Dakota	70.97	4.35	23.10	1.16
Lignite, Williston, North Dakota	72.68	5.11	19.74	1.31
Subbituminous, Montana	76.94	5.55	13.25	1.89
Coal, bituminous, Illinois, Franklin County	81.37	5.37	10.10	1.91
Coal, bituminous, Upper Freeport, Pa.	83.13	5.35	7.80	2.19
Coal, bituminous, Pittsburgh Bed, Bruceton, Pa.	84.57	5.39	6.94	1.72
Coal, bituminous, Alabama	86.54	5.42	5.13	1.54
Coal, bituminous, Somerset County, Pa.	88.59	4.53	2.57	1.35
Coal, bituminous, Tioga County, Pa.	88.98	4.86	3.08	1.62
Anthracite, Schuylkill County, Pa.	92.91	3.09	2.41	0.91

Ultimate analyses of the successive stages, in peat, brown coal, lignite, subbituminous coal, bituminous coal, semibituminous coal, and anthracite, therefore, show that extensive changes have taken place, the total result of which was a progressive elimination of volatile matters consisting of carbon dioxide, methane, water, and some carbon monoxide, in such relative proportions that there was a continuous larger loss of oxygen than carbon, with a loss of hydrogen that held the relative hydrogen content about constant throughout, except in the higher ranks, where considerable loss is notable.

CAUSES OF COALIFICATION

Practically little is known concerning the causes of coalification. Pressure is usually cited as the principal factor; time also is cited. But it

should be remembered that time is not a cause, only a factor of duration during which an agent has an opportunity to act. It is believed that slow spontaneous chemical changes are going on in most complex organic substances. During a short period such reactions would be but very slight, but over a period of thousands, or even millions of years, the total result must be considerable. It is possible that the decomposition reactions started in the vegetable debris in peat continues for a considerable time after the bog was covered, possibly together with other catalytic agencies. Under the same conditions, everything else remaining similar, the same results should be obtained in different deposits during the same length of time. Unfortunately there are no cases in which the conditions were the same. But let us consider briefly the time factor.

There are coals near Moscow, Russia, of Lower Carboniferous age, which must be ranked as lignites, of about the same rank as the lignites of North Dakota of Upper Cretaceous age. The German brown coals, of Oligocene age, still younger than the lignites of North Dakota, are only of a slightly lower rank than the Russian coal mentioned. If then the action set up by the enzymes of the biochemical stage, or spontaneous decomposition of the complex organic molecules, continued at all after the bog was covered, it did not continue very long, or the actions are so slow as to make very small differences during the millions of years that elapsed since the Carboniferous ages. Different causes must therefore be sought.

Pressure is generally cited by geologists as the cause. Looking over the field, many phenomena may be cited that appear to prove the assumption. Of the cases cited above, the Russian coals are covered with but a light overburden of rocks, unfolded and undisturbed; the German brown coals are covered with a light overburden consisting of clay; while the lignites of North Dakota are covered with a rather heavy overburden, but the rocks have not been disturbed or folded. Certain coals in the Alps of the same age as the Russian coals, but in rocks much folded and subjected to much earth movements, have been transformed to graphite and shungite. Coals of the Rocky Mountains of about the same age as the German brown coals, and again in rocks much folded, are of high bituminous rank. Following the lignites of North Dakota westward into regions more and more subjected to earth movements and earth thrusts with rocks folded more and more, are coals of the same age and of the same bed, transformed into coals of higher rank, being of high butiminous or even of anthracite rank in the Rocky Mountains. Many cases of like nature can be cited. In every case, such change occurs along areas of increasing marks of disturbance or folding, in rock that forms a heavy overburden. Also invariably coals of high rank, like the anthracite of eastern Pennsylvania, are associated with rocks that have been subjected to folding and earth thrust.

Rocks that have been folded are said to have been subjected to high pressure. There is therefore a good reason to assume that pressure is the factor that caused the devolatilization of coals or the changes of coals from a lower to a higher rank. But when pressure is considered from the standpoint of the physical chemist, the case becomes more complex. That pressure modifies or influences a chemical reaction is known. Pressure also brings about a chemical reaction in some cases when the volume of the products of the reaction are smaller than the original. It may also hasten the reaction under certain conditions, as in explosives and gases under pressure; but here other factors than pressure come in. But coals do not fall under any of these cases. The volume of the products of the reaction in coal is many times larger than the coal itself. Pressure could not have hastened any reaction started by reagents earlier.

Pressure is invariably accompanied by a rise in temperature, therefore, temperature should be considered briefly. When it is desired to hasten a reaction or start a reaction it is common practice to raise the temperature. It is known that rocks under higher pressure and in the act of folding, or where earth movements are taking place, are at a slightly higher temperature than the same rocks farther remote.[13] It is also known that, with increase in depth, the temperature rises even in undisturbed rocks. The temperature need not necessarily be high. A temperature only a few degrees higher of one deposit above that of another would show marked differences over a long period.

Loss of Moisture.—Along with the chemical change, there is a simultaneous decrease of moisture from approximately between 50 and 40 per cent., in the brown coals and lignite, to only a few per cent., in anthracite. In peat, the water is largely held colloidally, the humin matter being in typical state of hydrogel. With time the water is withdrawn, the mass becomes harder and more brittle as hydrogels do on dessication, the tendency being to develop into a solid similar to hard rubber. The total mass, of course, consists of a mixture of constituents; it is, therefore, not a pure hydrogel and will not transform into the hard solid form as it would if it were pure. The hardness or physical condition of a coal may therefore be accounted for by the colloidal nature of the ingredient matter. It required no high pressure nor high temperature to give it the characteristic physical condition in which coal is found. That it requires no high pressure nor high temperature to transform mature peat into a hard coal-like substance can be demonstrated easily in the laboratory. When thoroughly matured peat is slowly dried while kept under a slight pressure, so as to bring the components in close contact and keep out the air as the water is evaporated,

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[13] M. X. Stainier: Isogeotherms and Tectonic Geology. *Annales des Mines de Belgique.* Abst. *Coll. Guardian.* (1924) **127,** 415.

it will be converted into a hard coal-like substance. Any woody peat when treated with a weak alkaline solution and then left to dry slowly, will also be converted into a hard coal like substance.

Further, by proper means peat may be changed largely into a colloidal solution, which, on evaporation, gradually turns into a gel and, on further drying, into a mass that physically closely resembles bituminous coal. In like manner, brown coal, lignite, subbituminous coal, by proper means, may be brought into a colloidal solution from which it may be reverted by evaporation into mass that in many ways cannot be distinguished from the original coal, the one obvious difference from the original being that it has lost its banding or layering characteristic in coal.

If all the peat mass were in a typical stage of hydrogel, no pressure would be required in order that peat be transformed into a hard coal-like substance after gradual elimination of water. But as already stated, peat consists of a mixture of substances, many of which are not complete hydrogels; spaces exist between the different components requiring external pressure to bring the different parts together, and if none is applied on dessication the mass dries into a more or less spongy mass. If, however, but slight pressure is applied, just enough to keep the spaces from filling with air as the water is removed, a hard bony mass results. A heavy overburden should, therefore, have the tendency to produce a solid compact coal.

Effect of Overlying Rocks.—These laboratory experiments are corroborated in nature. The German brown coals have relatively but a light overburden. They are of a loose spongy nature, still much like peat. American lignites of the same age, on the other hand, were provided with a heavy overburden and have been subjected to considerable pressure. This resulted in a compact dense black coal termed lignite, in contradistinction to the German brown coal. Microscopically the German brown coals and American lignites do not differ essentially; the kind of components are quite similar in each, their origin was therefore quite similar. Their ultimate analyses generally does not differ much, yet in some ways, such as outward appearance and physical structure, they differ considerably. With the chemical changes and the changes in moisture content, there has also taken place a gradual change in physical condition of the coal.

All constituents of peat are colloids in one form or another; the humic components in particular are in a state of hydrogel. That means that relatively a large amount of water is present as an inherent part of the mass. Water is so closely associated with the peat substances that it cannot be said where the one begins and the other ends as a part of it. The solid colloidal particles composing the gel are relatively far apart; this is characteristically seen under the microscope. As the elimination of water proceeds, these particles are brought closer and closer together

through internal pressure. In lignites, still containing as much as 50 or 40 per cent. water, each ultra particle of coal matter must be surrounded by a film of water which is, however, so thin that it is not visible under the microscope, and is therefore not apparent. Yet the ultimate coal particles are still relatively far apart. The mass is still loose in texture but not porous in the usual sense, but is soft. In the subbituminous coals, where water has been eliminated still further, the ultimate particles have been brought still closer together, and the mass is correspondingly more compact. In the bituminous coals, moisture has now been reduced to within between say 3 and 8 per cent. The water in the coal under such conditions, or in other words the moisture surrounding each ultra particle, can no longer be present in minute droplets or films but can only be present in a molecular state in order to be uniformly distributed. Yet the ultimate particles, although now much closer together than in peat or brown coal, are still relatively far apart, but the spaces between these can no longer be filled with water but must be filled by gases.

Change in Physical Appearance after Loss of Moisture.—Parallel with the loss of moisture, is to be noted a change in the physical appearance of coals. Lignites have a characteristic granular appearance under the microscope. The granular condition changes more and more into a glassy or vitreous condition as coals of higher rank are reached and reaches a maximum in the coking coals. Coking coals, as a rule, have a characteristic vitreous appearance.

At the end of the coalification process, the various constituents that entered into the peat deposit, though still recognizable, are now in a chemically and physically changed condition, as may be accounted for by biological and coalification processes.

Composition of Coal

All the components recognizable in peat may be traced with certainty from the peats through the whole series of coals such as brown coal, lignites, subbituminous coals, bituminous coals, and anthracite. These components in peat, to repeat, may be summed up as follows:

1. The larger components derived from the woody parts of plants, such as stems, branches, roots, more or less whole or in larger fragments (Fig. 3).

2. The smaller components derived from the same plant parts but more highly fragmented (Figs. 3 and 4).

3. The attritus is composed of (*a*) finely macerated matter derived from the woody parts of plants; (*b*) finely macerated matter derived from other carbohydrate plant substances like pith, cortex, bark, leaf-tissues, gums, etc.; (*c*) cuticular matter; (*d*) spore and pollen matter; (*e*) resinous matter; (*f*) waxy and fatty matter; (*g*) other degradation matter; and (*h*) mineral matter (Fig. 4).

The larger pieces corresponding to peat wood are abundantly found in the brown coals and lignites and are easily recognizable as such, either microscopically through thin sections or macroscopically (Figs. 11 and 12).

In the lignites, they are recognized as black, glistening, more or less lenticular masses. They are generally spoken of as "bright coal." Generally their outward appearance betokens that of woody fragments. When examined microscopically in thin sections, no doubt remains that they actually represent pieces of wood. Being derived from wood, they are called anthraxylon (Fig. 12).

Samples of typical earthy brown coals from the Riebeck mine in Germany were recently examined by the author. These samples showed that they differed in no respect in composition and origin from American lignites (Fig. 11). In the subbituminous coals, anthraxylon is likewise prominent and easily recognizable as woody components (Fig. 13). They are here, however, thinner and more compact; in other words, they have been more compressed or flattened. The subbituminous coals offer a fortunate transition stage from lignite to bituminous coal. This provides a means to recognize components definitely in the bituminous coals, although without this transition the anthraxylon is easily and clearly recognized in the bituminous coals (Fig. 14). From the general appearance and banded nature of anthracite, it has long been assumed that anthraxylon is also present in these. Recent methods of polishing and edging have definitely proved this assumption to be correct.

The smaller or more fragmentary woody component of peat can also be traced easily and definitely from one end of the series to the other. These are called smaller anthraxylon components. Their origin and structure differ in no way from the larger (Figs. 15, 16, and 17).

The smaller anthraxylon strips and the attritus together ordinarily comprise the dull coal (Figs. 18, 19, and 20). But when a number of the smaller anthraxylon strips are packed closely together with none or but little attritus between them, they also constitute bright coal (Figs. 21, 22, and 23).

The thickness of the anthraxylon units varies greatly in any coal. In general, their thicknesses decrease with the rank of the coal, being most massive in the lignite, where they have suffered the least compression, and where they may be six inches or more in thickness, and thinnest in the anthracite, where they have suffered the most thorough loss of volatile matter and compression. But in any coal all conceivable sizes and thickness are met with, from those many feet long, several feet wide, and several inches in thickness to a microscopic size. Some coal beds are composed of a large proportion of anthraxylon, these are anthraxylous coals; in others the proportion is much smaller and the attritus forms the larger part of the coal; these are attrious coals. In some, these components are largely quite thick; in others, like the Pittsburgh bed, they are mostly relatively thin.

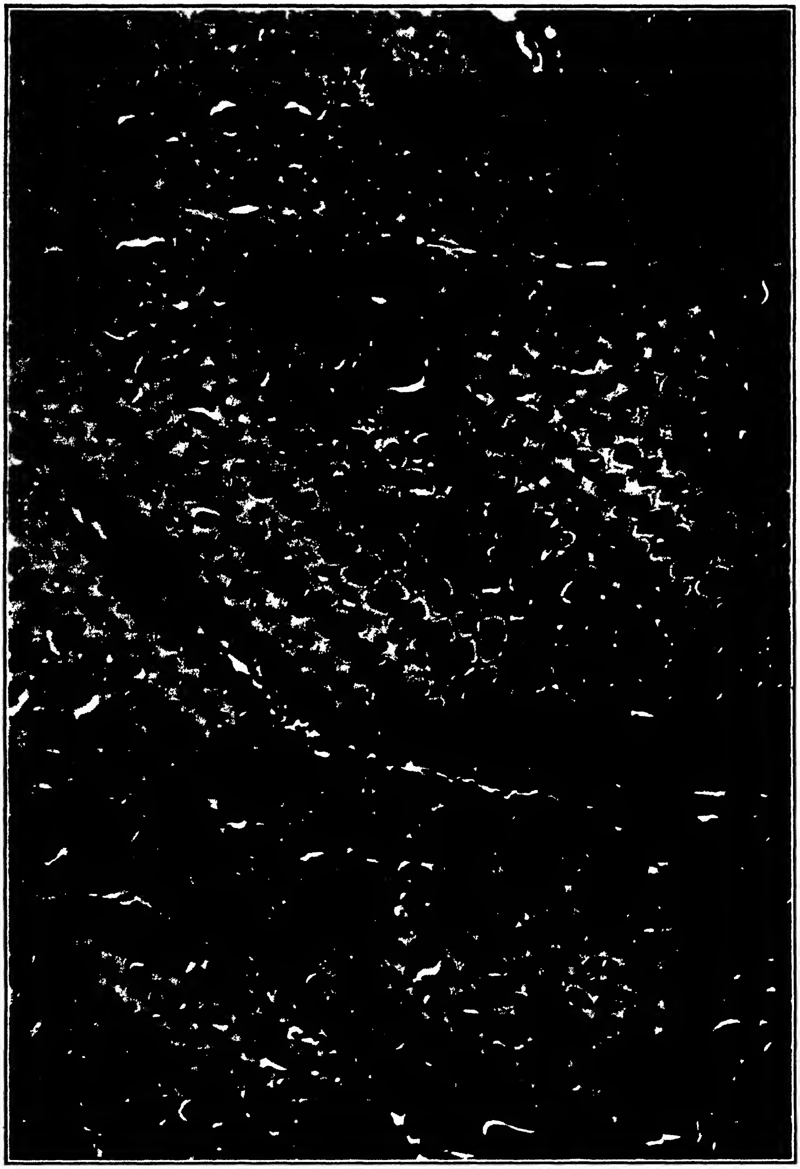


FIG. 11.—THIN CROSS-SECTION OF ANTHRAXYLON OF EARTHY BROWN COAL FROM RIEBECK MINE, GERMANY; STRUCTURE IS THAT OF A CONIFER; CELL WALLS OF FIBERS ARE FAIRLY WELL PRESERVED THOUGH CONSIDERABLY COMPRESSED; ANNUAL RINGS OF TREE ARE WELL SHOWN. × 200.

FIG. 12.—THIN CROSS-SECTION OF ANTHRAXYLON OF LIGNITE FROM WILTON, N. DAK.; AUTUMN WOOD IS WELL PRESERVED WHILE SPRING WOOD IS IN MORE ADVANCED STAGE OF DECAY; BLACK PATCHES AND HEAVY BLACK LINES REPRESENT RESIN. × 200.

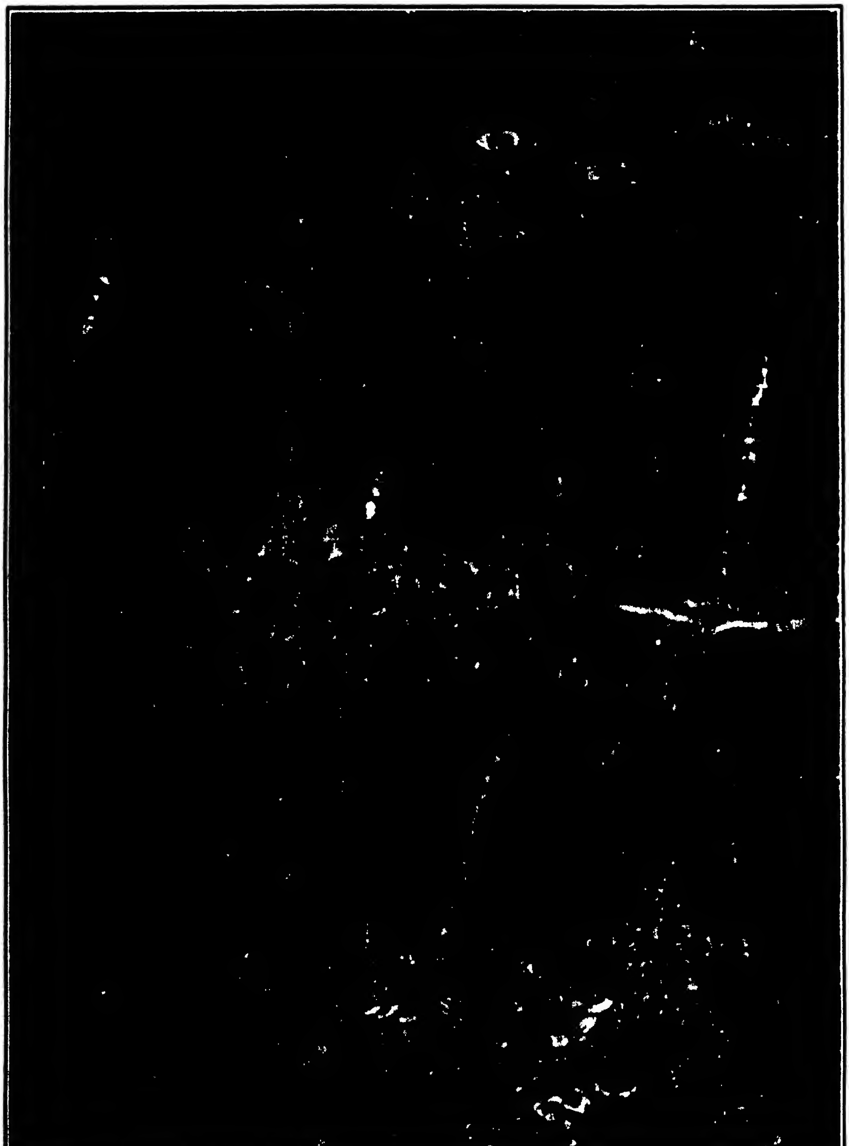


FIG. 13.—THIN CROSS-SECTION OF ANTHRAXYLON OF SUBBITUMINOUS COAL FROM MONTANA; AUTUMN WOOD IS FAIRLY WELL PRESERVED, SPRING WOOD IS IN MORE ADVANCED STATE OF DECAY; THE MASS IS MORE COMPRESSED AND MORE COMPACT THAN THAT OF LIGNITE SHOWN IN FIG. 12. × 200.

FIG. 14.—THIN CROSS-SECTION OF ANTHRAXYLON OF BITUMINOUS COAL FROM THICK FREEPORT BED; WOODY STRUCTURE INCLUDES CONSIDERABLE RESIN, SHOWN WHITE. × 200.

FIG. 15.—THIN CROSS-SECTION OF DULL COAL OF BROWN COAL FROM RIEBECK MINE, GERMANY; THIN STRIPS OF ANTHRAXYLON ARE EMBEDDED IN ATTRITUS; ATTRITUS IS COMPOSED OF WOODY DEGRADATION MATTER, CUTICULAR MATTER, SPORE AND POLLEN MATTER, RESINOUS MATTER, AND CHARRED WOODY MATTER, SHOWN BLACK. × 200.

FIG. 16.—THIN CROSS-SECTION OF DULL COAL OF LIGNITE FROM SHERIDAN, WYO.; THIN STRIPS OF ANTHRAXYLON ARE SHOWN EMBEDDED IN ATTRITUS; ATTRITUS IS COMPOSED OF WOODY DEGRADATION MATTER, MUCH CARBONIZED MATTER, SOME SPORES AND POLLENS, AND A SMALL AMOUNT OF RESINOUS MATTER. × 200.

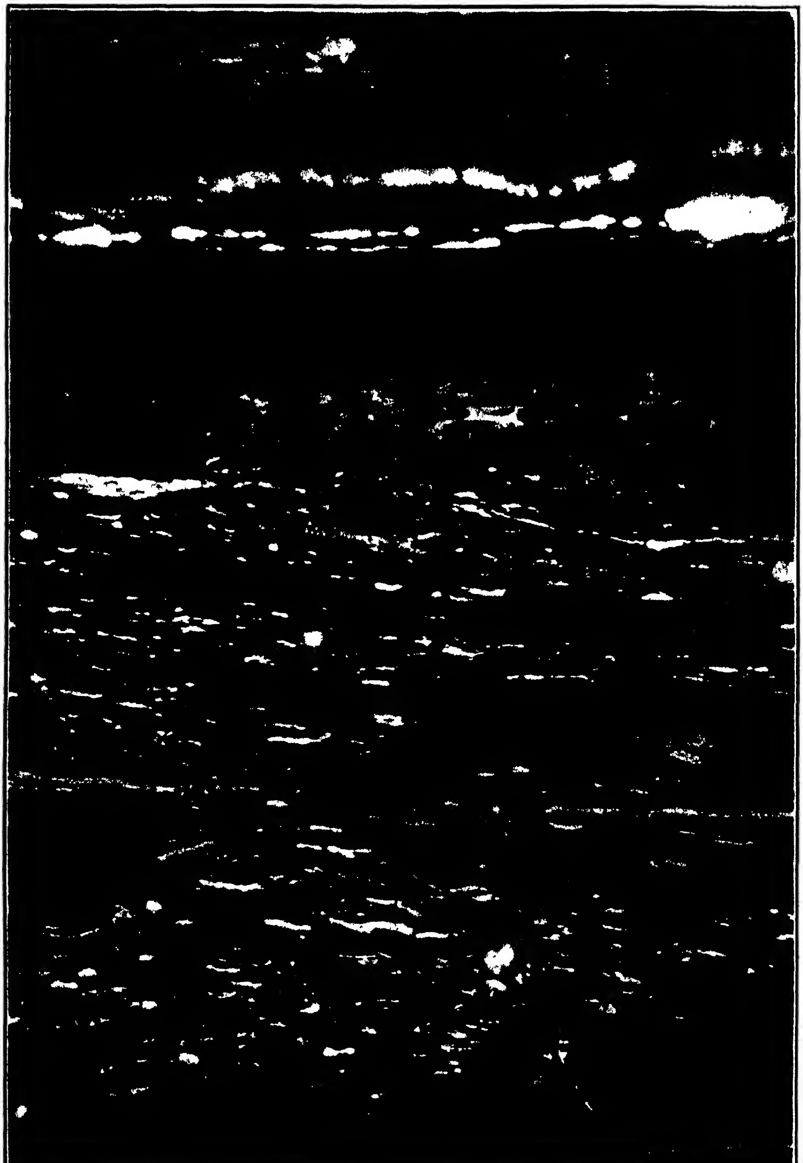


FIG. 17.—THIN SECTION OF DULL COAL FROM A BITUMINOUS COAL FROM THICK FREEPORT BED; THIN STRIPS OF ANTHRAXYLON, ONE OF WHICH CONTAINS WELL-PRESERVED STRUCTURE, ARE EMBEDDED IN ATTRITUS; ATTRITUS IS COMPOSED OF WOODY DEGRADATION MATTER, SPORES, CARBONIZED AND SOME CUTICULAR MATTER. × 200.

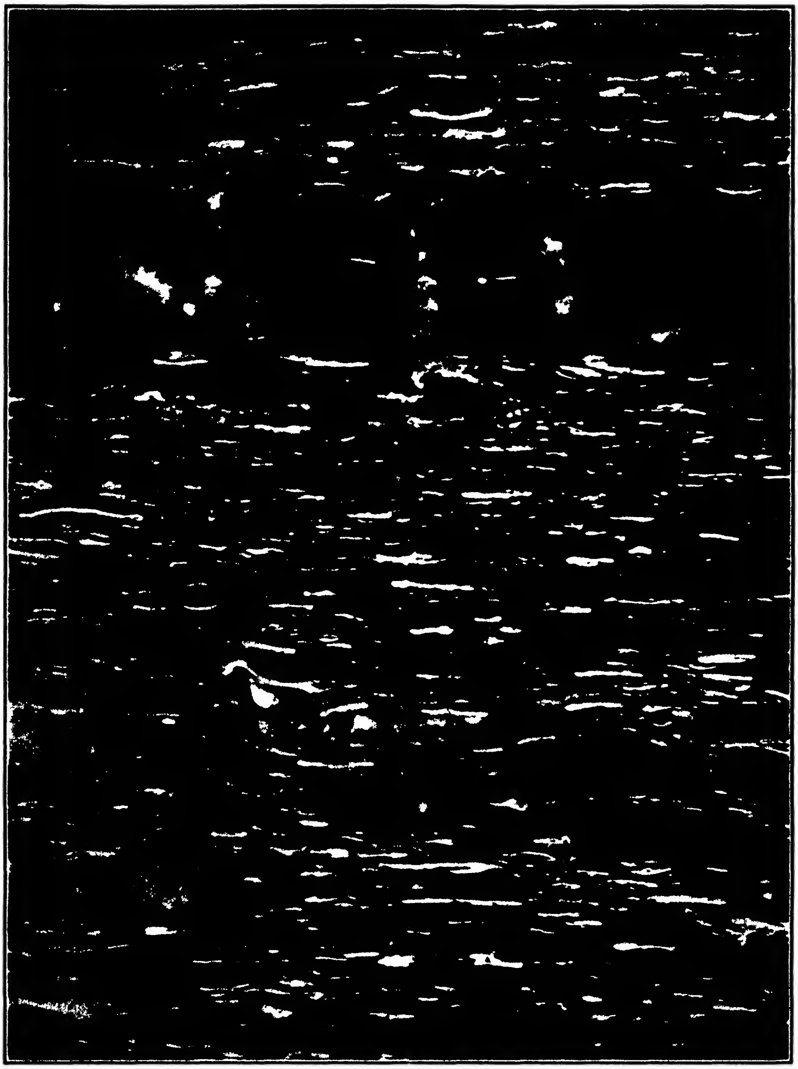


FIG. 18.—THIN CROSS-SECTION OF DULL COAL OF A BITUMINOUS COAL FROM THICK FREEPORT BED; LARGER PART CONSISTS OF ATTRITUS WITH BUT A FEW THIN STRIPS OF ANTHRAXYLON; ATTRITUS IS RICH IN SPORES. × 200.

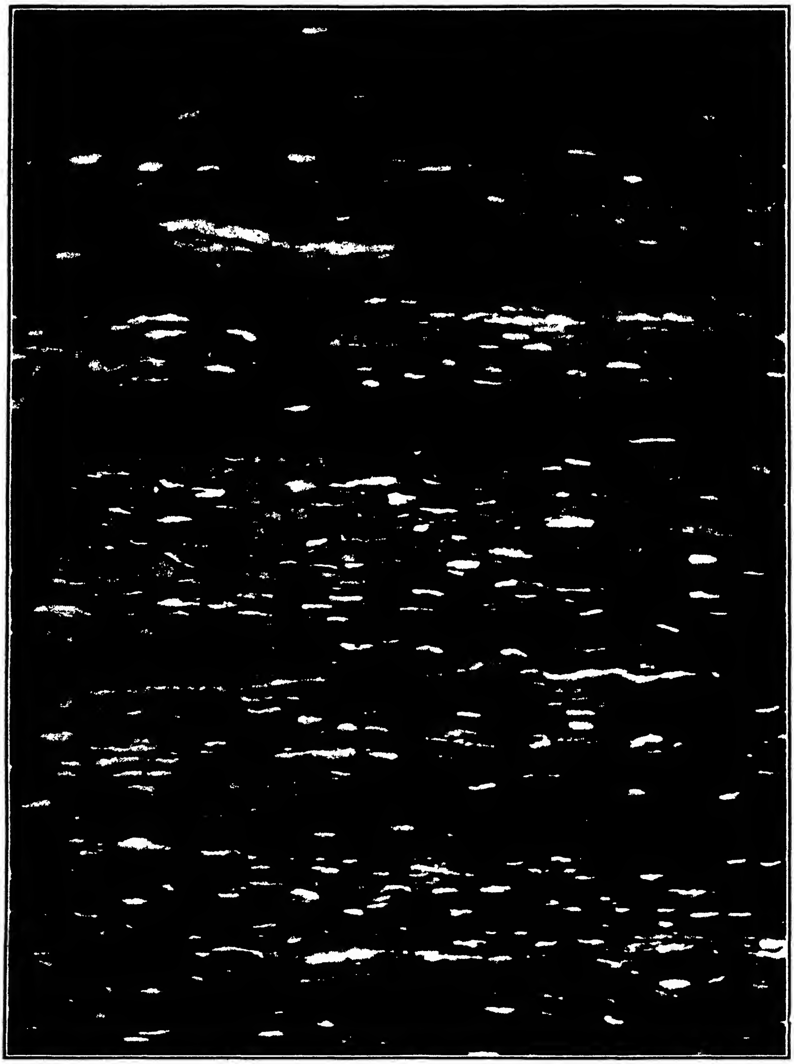


FIG. 19.—THIN CROSS-SECTION OF DULL COAL OF BITUMINOUS COAL, UPPER FREEPORT BED, CANNELTON, PA., SHOWING STRIPS OF ANTHRAXYLON; ATTRITUS IS COMPOSED LARGELY OF WOODY DEGRADATION MATTER, RELATIVELY FEW SPORES, AND SOME RESINOUS MATTER. × 200.

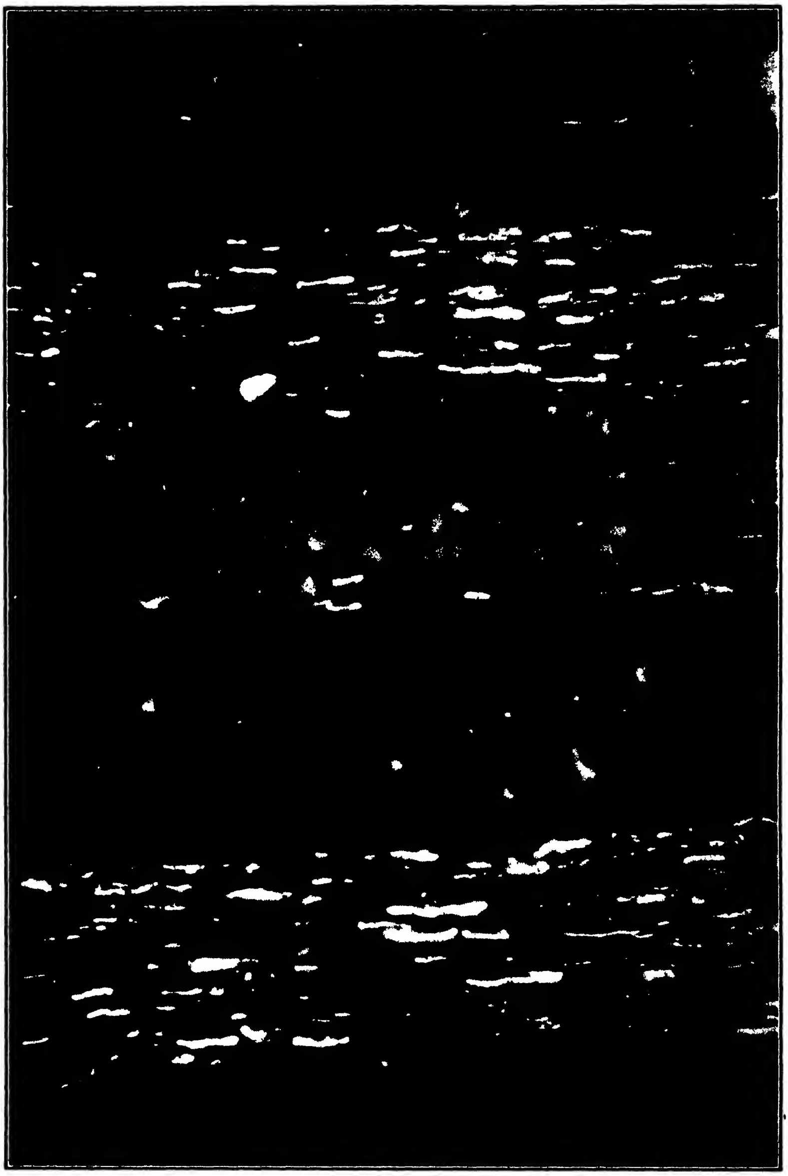


FIG. 20.—THIN CROSS-SECTION OF BITUMINOUS COAL, UPPER FREEPORT, WITH NUMBER OF THICKER STRIPS OF ANTHRAXYLON INTERLAYERED WITH AN ATTRITUS RICH IN SPORES; THERE IS ABOUT AN EQUAL PROPORTION OF ANTHRAXYLON AND ATTRITUS IN THIS LAYER, BUT IT STILL MAY APPEAR AS DULL COAL. × 200.

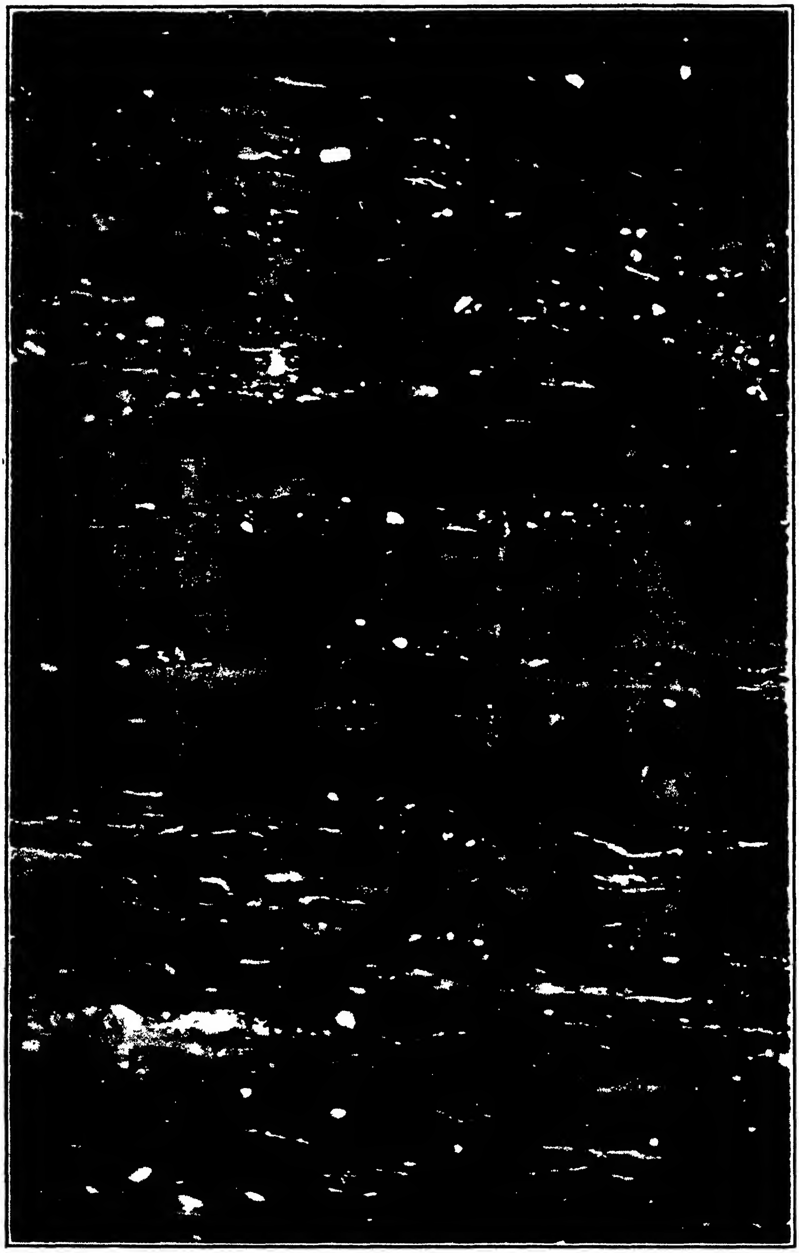


FIG. 21.—THIN CROSS-SECTION OF BITUMINOUS COAL, PITTSBURGH COAL; LAYER CONTAINS LARGER PROPORTION OF THIN ANTHRAXYLON STRIPS THAN ATTRITUS AND APPEARS AS BRIGHT COAL. × 200.

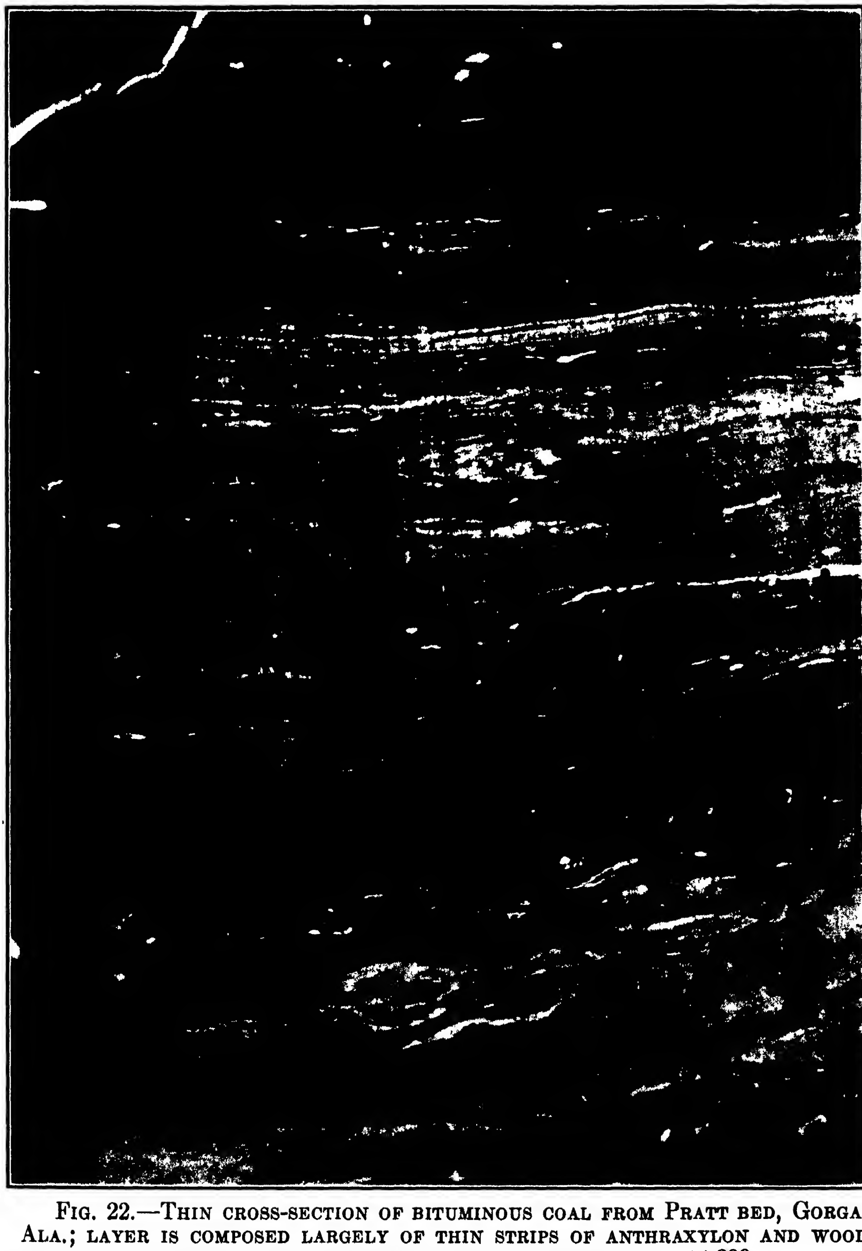


FIG. 22.—THIN CROSS-SECTION OF BITUMINOUS COAL FROM PRATT BED, GORGAS, ALA.; LAYER IS COMPOSED LARGELY OF THIN STRIPS OF ANTHRAXYLON AND WOODY DEGRADATION MATTER AND APPEARS AS A TYPICAL BRIGHT COAL. $\times$ 200.

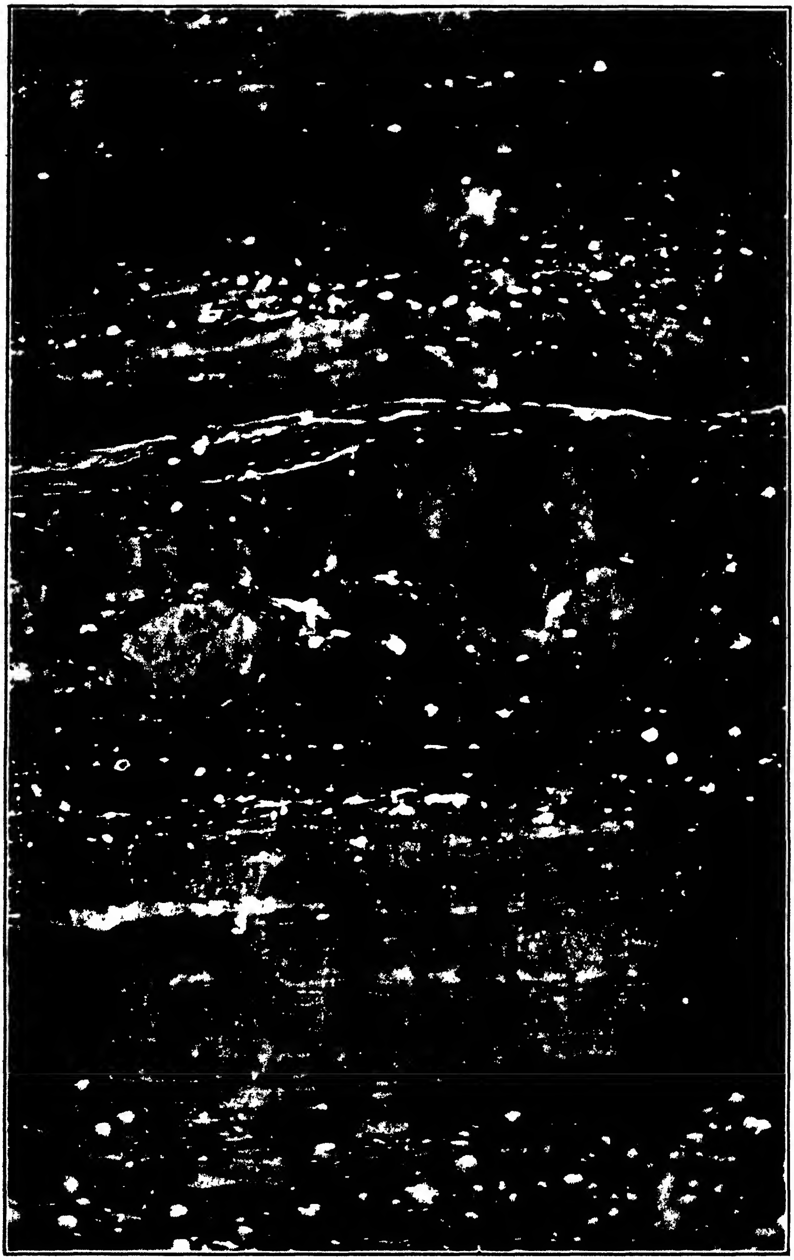


FIG. 23.—THIN CROSS-SECTION OF BITUMINOUS COAL, REDSTONE BED, MADISON, PA.; LARGER PART OF LAYER IS COMPOSED OF STRIPS OF ANTHRAXYLON AND WOODY DEGRADATION MATTER AND HAS APPEARANCE OF BRIGHT COAL. × 200.

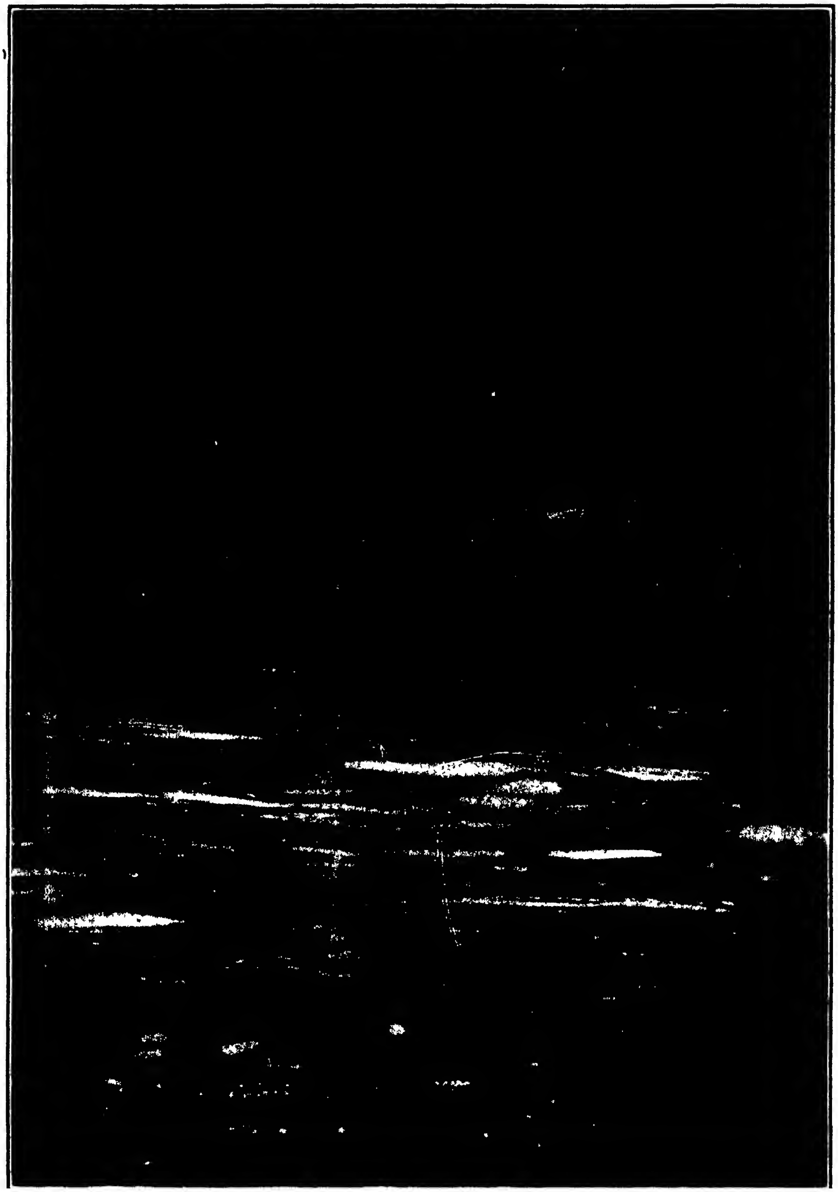


FIG. 24.—THIN CROSS-SECTION OF ANTHRAXYLON OF A BITUMINOUS COAL, UPPER FREEPORT, WITH RESINS INCLUDED IN CELLS. × 200.

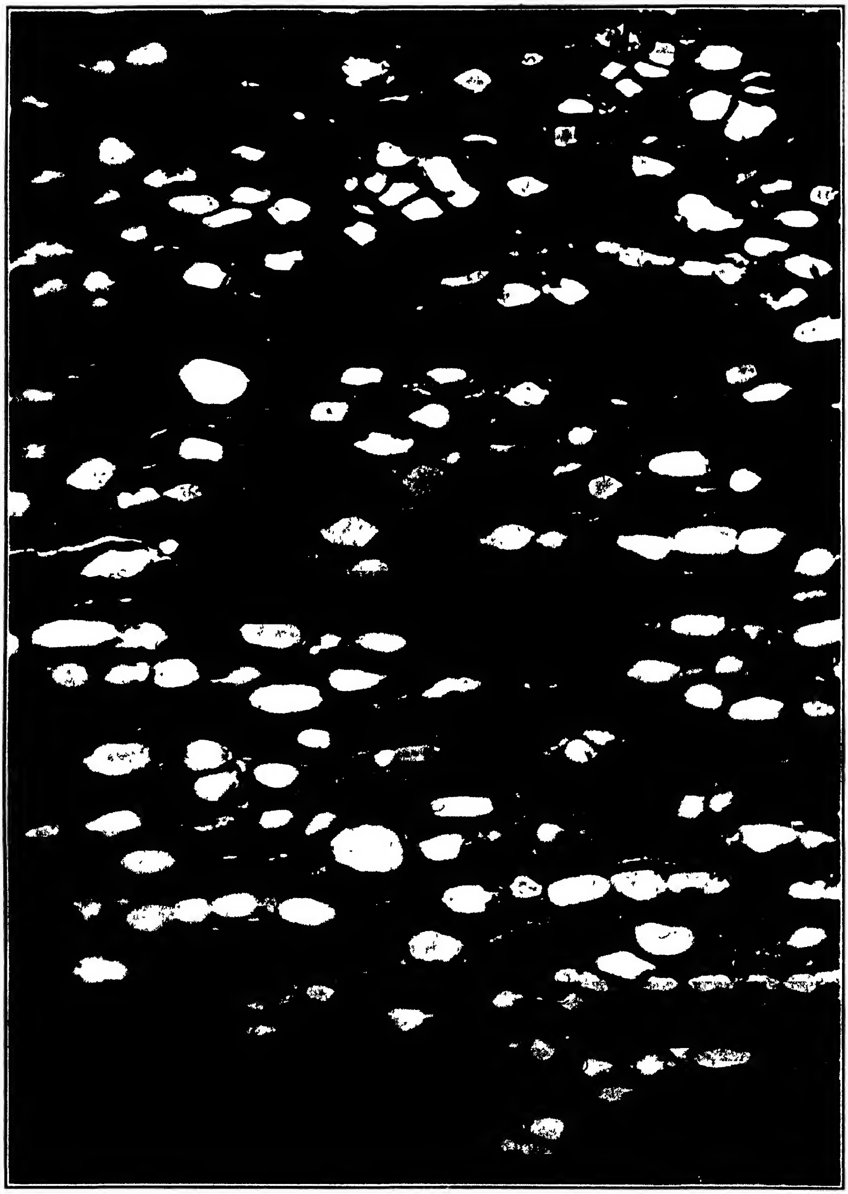


FIG. 25.—THIN CROSS-SECTION OF ANTHRAXYLON OF A LIGNITE FROM SHERIDAN, WYO., INCLUDING RESIN. × 200.

FIG. 26.—THIN CROSS-SECTION OF ATTRITUS OF BROWN COAL FROM RIEBECK MINE, GERMANY; ATTRITUS CONTAINS ALL CONSTITUENTS FOUND IN PEAT, LIGNITE, SUB-BITUMINOUS, AND BITUMINOUS COAL, BUT IS NOT AS COMPACT AS THAT OF OTHER COALS. × 200.

Fig. 27.—Thin cross-section fo attritus from a North Dakota lignite; composed largely of woody degradation matter, some pollen matter, resinous particles, cuticles, carbonized matter, and pyrite. × 200.

FIG. 28.—THIN CROSS-SECTION OF ATTRITUS OF SUBBITUMINOUS COAL FROM KEMMERER, WYO. × 200.

FIG. 29.—THIN CROSS-SECTION OF ATTRITUS OF A BITUMINOUS COAL, INCLUDING A FEW THIN STRIPS OF ANTHRAXYLON. × 200.

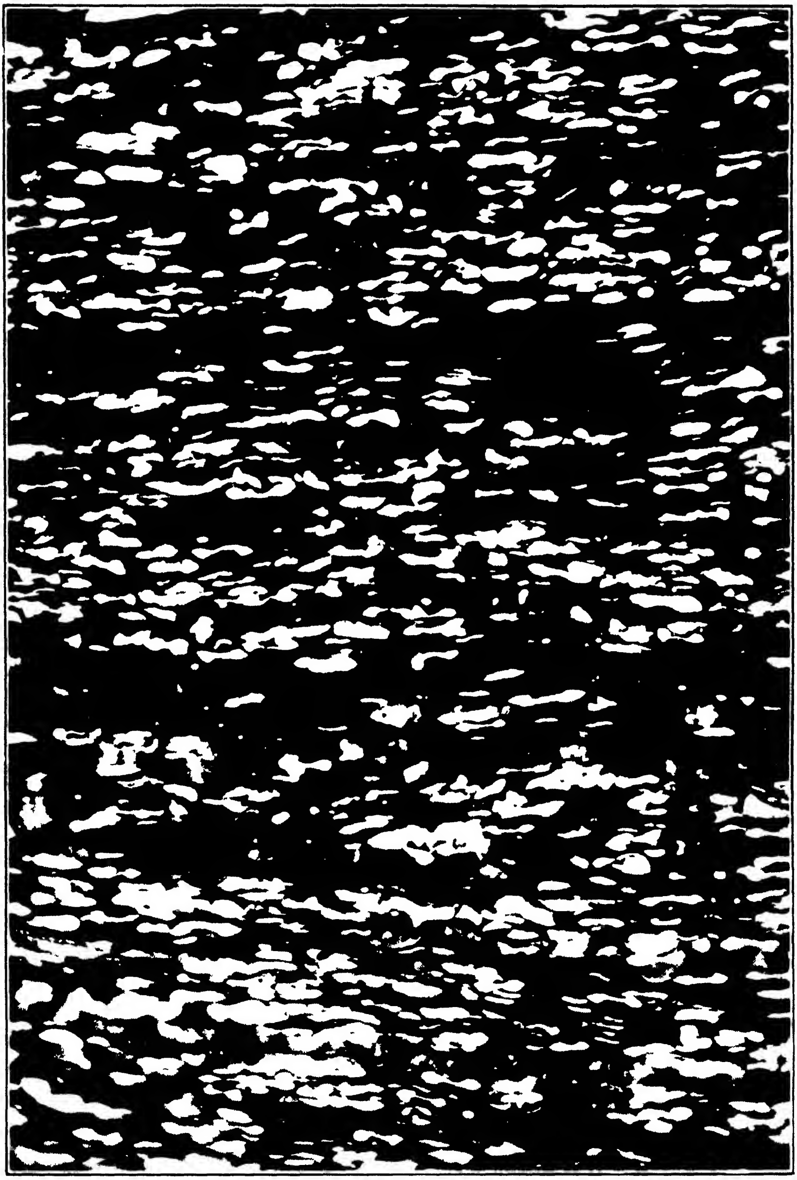


FIG. 30.—THIN CROSS-SECTION OF ATTRITUS OF A BITUMINOUS COAL, LOWER KITTANNING BED, RICH IN SPORE MATTER; SPORES ARE CHARACTERISTIC SPORES OF LOWER KITTANNING BED.

Remains of the original woody structures are preserved in all anthraxylon; in some they are exceptionally well preserved, in others but faint traces are left. The state of preservation again varies, in general, directly with the rank of the coal. The most and the best-preserved structure has been retained in the lignites, and from here drop off until the anthracites are reached. The state of preservation is, however, not always determined by the metamorphism of the coal. In many cases, it was probably determined during the first part of the peat stage.

Original and natural cell contents, such as resin, are commonly included (Figs. 14, 24, and 25). Resinous matters are not decomposable and have retained much of their original bulk, and while the woody fragments enclosing them have largely decomposed, the resinous contents have been concentrated in them, and often form the larger part of the anthraxylons. This is particularly well known in the lignites, in which resin-bearing conifers were the main contributors.

The attritus constitutes the embedding medium and in a cross-section appears between the thinner anthraxylon as layers alternating with it. The attritus and the smaller anthraxylon strips together constitute the dull coal, but the attritus alone also has the appearance of a dull coal. Cannel coal, for example, is all attritus and has a dull appearance.

Although a complex substance, the attritus as a whole, and the main constituents composing it, can be traced from one end of the series to the other, clearly and definitely. It consists largely of the rubbish or refuse that escaped complete decay. It would be expected, therefore, to find in it besides the woody degradation matters, many of the substances more or less resistant to decay. To these substances belong the cuticles or outer coverings of leaves, stems, and branches; and the waxy fatty and resinous coverings, pollen grains and spores; also resinous, waxy and fatty contents of cells and tissues. Besides these, there is a long list of substances in plants that are more or less resistant to decay, such as tannins, alkaloids, terpenes, camphors, and others. Many of these are so finely dispersed throughout the plant, and now through the attritus, that they escape observation under the microscope. Many of these are probably absorbed by the coal matter itself (Figs. 10, 26 to 30).[14]

Summary

In a study of coal, all evidence points to the fact that coals have been formed in a similar manner as have the peat beds of today; with

[14] For supplementary illustrations on origin and composition, the reader is referred to the following articles by the author: Structure in Paleozoic Bituminous Coals. Bur. of Mines *Bull.* 117 (1920)—Compilation and Composition of Bituminous Coals. *Jnl. Geol.* (1920) **28,** 185–209—Constitution of Coal Through a Microscope. *Proc.* Coal Min. Inst. Amer. (1919) 34–35—Recent Developments in Microscopic Study of Coal. *Proc.* Coal Min. Inst. Amer. (1920) 88–119. Reprinted in *Coal Age* (1920) **18,** 1183–1189, 1275–1279 and **19,** 12–15—The Origin and Constitution of Coal.

that as a basis, the study of peat is essential. In turn, for the study of peat, considerable knowledge of the chemistry of plants and of decay is essential.

The components and products of plants have been outlined, a brief review of the mechanism of decay given, and the decay of wood reviewed.

The purpose of this paper is to show that all the plant products went into the peat bog, but an elimination of certain components and a concentration of others took place through decay; that cellulose, although constituting the bulk of the plant body, did not contribute materially to the bog in verification of Fischer's[15] theory, and that many of the byproducts of coal distillation are recognized in the plant products of the living plant.

The plant parts and plant products remaining at the close of the biochemical processes are distinctly recognizable; but little is known of the chemical composition of most of these. The ultimate analysis shows that during the biochemical processes, a relatively larger loss of oxygen than carbon took place, resulting in a relative increase in carbon and a relative loss in oxygen while the hydrogen content remained constant. This relative progressive change of the carbon and oxygen content began during the biochemical stages, and continued during the successive changes into brown coal, lignite, subbituminous coal, bituminous coal, and anthracite. These changes are called coalification.

All of the components of peat, definitely recognizable, may be traced clearly and definitely through the whole series of coals from brown coal to anthracite.

The larger woody components of peat, when coalified, partake of a bright shiny appearance and have popularly been called bright coal. Such units being derived from wood are called anthraxylon. The smaller fragments of woody matter in peat, when coalified, also partake of a bright shiny appearance and are easily visible in the coals at close examination or with a hand lens. These have the same origin and the same structure as the larger components and are called the smaller anthraxylon. The attritus of peat, on coalification, partakes of a dull appearance and gives rise to dull coal.

Coal comprised of a mixture of the smaller anthraxylon and attritus constitutes a dull coal, the dull coal of popular usage. A number of smaller anthraxylon constituents when including but a relatively small

Proc. Wyoming Hist. and Geol. Soc. (1924); also to the Origin of Coal, by White and Thiessen, with a chapter by Davis on formation of peat. Bur. of Mines *Bull.* 38 (1914)—Microscopic Study of the Freeport Coal Bed, by Thiessen and Vorhees. *Bull.* 2, Carnegie Inst. Tech. (1922)—Correlation of Coal Beds in the Monongahela Formation, by Thiessen and Staud. *Bull.* 9, Carnegie Inst. Tech. (1923)—Correlation of Coal Beds in the Allegheny Formation, by Thiessen and Wilson. *Bull.* 10, Carnegie Inst. Tech. (1924).

[15] Franz Fischer und Hans Schrader: Enstehung und chemische Struktur der Kohle. 2d. ed. Verlag von M. Gerardif, Essen, 1922.

amount of attritus also comprises a bright coal. The terms "bright" coal and "dull" coal are merely relative terms. Anthraxylon and attritus, on the other hand, are definite terms.

DISCUSSION

Edward C. Jeffrey,* Cambridge, Mass.—Do I understand that the charcoal found in recent lacustrine deposits is due to bacterial action?

Reinhardt Thiessen.—Yes; secondarily because bacteria need oxygen, this deprives peat of its oxygen which then becomes a reducing agent.

Edward C. Jeffrey.—How is it then that in a recent deposit of that kind there were charred and uncharred branches of trees intermingled with one another, all subject to the same influence under water cover? I find it difficult to understand that situation otherwise than as the result of charred twigs and uncharred.

Reinhardt Thiessen.—I still have my troubles with that theory.

Ralph H. Sweetser,† Columbus, Ohio.—This past year I examined "mother coal" in the No. 2 gas seam, in West Virginia, and in the No. 6 and No. 7 coal seams in Kentucky. I do not think there is any resemblance between the two. It was stated this morning that possibly the partings in coal came from volcanoes; is it not possible that the carbon itself might have been deposited in the same way on top of the coal seam?

Reinhardt Thiessen.—All the charcoal that I have examined shows plant structure, even small fragments found in the thin sections. They are not what may be called amorphous carbon, such as is produced by natural gas when burned in contact with a cold surface.

David White,‡ Washington, D. C.—This hypothesis to account for fusain carries the idea of smothered decomposition. A difficulty lies in the occasionally great thinness and the great extent and the frequency of occurrence of the fusain partings. The same troubles attend Doctor Ashley's explanation.

Reinhardt Thiessen.—Although we hear so much about putrefaction and different kinds of decay, there is only one kind. Bacteriologists recognize, of course, anaerobic and aerobic decay, the difference being that aerobic decay can take place in free oxygen while in anaerobic decay the oxygen is not freely accessible; but as far as chemical decomposition is concerned the result is the same. There is also to be dis-

* Professor of Botany, Harvard University.

† Assistant to First Vice-president, American Rolling Mill Co.

‡ Senior Geologist, U. S. Geological Survey.

tinguished between hydrolysis, splitting of the molecule into soluble compounds, and fermentation, in which the split products are further decomposed to furnish energy in the bacteria. Bacteria live on many insoluble substances. These they first split into soluble parts, which then diffuse into their bodies where they are digested.

Edward C. Jeffrey.—The author has shown the tops of peat bogs. Obviously he had in his mind what others have called the landing stage of a low moor, that is a moor that was originally water and later was covered by forests. Investigations of the United States Geological Survey (or the Bureau of Mines, I do not recall which) show that 90 per cent. of the vegetable accumulations in the United States that have been investigated are laid down in open water. In other words, they are not of the nature that the author has described. Thomia has come to the same conclusion in Germany.

The author has shown side by side on the same slide, dark resin and light colored resin. Of course the geological age would have a good deal to do with the interpretation made of the slide, but the capacity for producing and continuing resin internally was developed only lately. The earlier plants were not able to produce resin in their cells. Any occurrence of resin, other than in Paleozoic forms inside cells, would be highly under suspicion.

In one section shown there were two remarkable things. One was the materials of resin inside the cells, which would be impossible; the other, that the resin, in the same proportion, was quite black in one case and light colored in the other. I have examined a great deal of amber from Mesozoic deposits and it is a very uniform substance and is always light colored.

Reinhardt Thiessen.—The black appearance on the screen of these resinous parts is not necessarily as dark in the section as it would appear; to bring them out color screens were used.

Edward C. Jeffrey.—A great many of the things interpreted as resin were simply the uncollapsed tracheids. I have often seen them. They are individual tracheids that do not collapse.

Reinhardt Thiessen.—I do not believe that that is possible; I have gone into that matter thoroughly and I am convinced that those are actually resin inclusions.

Edward C. Jeffrey.—All resin cells in Mesozoic wood are dark colored.

David White.—The paper emphasizes two or three outstanding points. One is the lack of initial differences between a peat of a given type and that of a lignite, subbituminous or bituminous coal, or anthracite of the same type.

The author shows splendid technique in bringing out the cell structure in material in which it has not so successfully been shown before. He leaves no escape from the fact that most coals have a great amount of wood in them and are laid down where a great amount of woody vegetation grew, more or less of which decayed according to the conditions prevailing from time to time. Consequently, the deposit varies as to the concentration of resins and other decay-resistant materials.

The Microstructure of Coal

By Clarence A. Seyler* Swansea, Wales

(New York Meeting, February ,1925)

The technical difficulties of cutting thin sections of coal for examination by transmitted light have hitherto restricted the investigation of the important subject of the microstructure of coal to the few possessed of the requisite skill and time. Apart from this, the method fails with anthracites and other coals rich in carbon, owing to the opacity of the material. Occasional use of the method of polishing a surface, with or without etching, has been made, but it was not until Winter[1] published an account of his results that attention was seriously directed to the method.

In May, 1923, a specimen of dull anthracite came into my hands; I tried Winter's method on it and the presence of megaspores and other vegetable structures became clearly visible. A preliminary notice was published by me;[2] but I soon abandoned the use of Schulze's solution, having found that a mixture of chromic and sulfuric acids gave far better results. In the meantime Turner and Randall, in America, had independently developed the method of flame etching, as applied to anthracite, with great success. I have spent a year studying the method of chromic etching, which gives excellent results with bituminous coals and cannels, as well as with anthracite. For anthracites, I have used the chromic method and Turner's method of flame etching, whichever was the more convenient or as a check one on the other.

The polishing is done, according to metallurgical practice, by the use of a polishing machine and successively finer emery paper, followed by polishing on cloth moistened with a suspension of levigated green oxide of chromium, and a final rubbing on "selvyt" (a cotton velvet polishing cloth) moistened with alcohol. The polished sample is examined by reflected light with a $\frac{2}{3}$ and $\frac{1}{6}$ in. objective. Bituminous coals usually show considerable structure, and even anthracites show it faintly in places. The sample is then etched by immersion in a boiling solution made by adding 10 c.c. of concentrated sulfuric acid to 30 c.c. of a saturated solution of chromic acid; enough water is then added to dissolve

* Public Analyst.

[1] *Fuel in Sci. & Prac.* (1923) **2**, 21 and 78.

[2] *Fuel in Sci. & Prac.* 1923) **2**, 217.

any precipitated chromic acid. The solution is boiled until chromic acid begins to separate and the polished sample is then immersed in the liquid, which is kept boiling for a few minutes. The sample is then removed, cooled, washed, dried, and very slightly rubbed on selvyt moistened with alcohol. Anthracites require from three to five minutes, bituminous coals usually less than one minute. The etching can be carried out in successive stages.

The method appears to offer several advantages over that of sectioning. It is applicable to all kinds of coal and is quick and easy. So far as my experience goes, it shows the presence of structure as well as the thinnest sections. Indeed, since very thin sections are difficult to prepare, whereas in the polished specimen one has a section of infinitesimal thickness, it is possible to use very high magnifications and to bring out details of structure that otherwise would escape us.

The interpretation of the results, especially owing to the difference between transmitted and reflected light, requires experience. As Stopes and Wheeler[3] have said, we must educate a new race of paleobotanists trained to perceive in minute fragments of cells "a recognizable plant structure." To this task of self education, my endeavors have been chiefly devoted, before entering on the systematic study of the Welsh coal field. Miss M. Evans, working under the direction of Doctor Wheeler, is applying the method to the Yorkshire coal field with very promising results.

The chief aim of the investigation is the attempt to infer from the results observed: (1) The plant tissues from which the coal has originated or which have contributed to it. The chief tissues are distinguished by marked differences of chemical composition and resistance to decay. Thus in woody tissue one might expect the pectocelluloses (such as constitute the middle lamellæ of cells) to decay rapidly, while the lignocellulose would persist longer. The cortex would probably behave somewhat differently but the cutinized and suberized portions, such as spore exines, cuticle, and cork are richer in hydrogen and would probably resist decay longer and yield a different coal. We wish to know whether we can infer from the observed fragments, the tissues (xylem, cortex, cork, cuticle, or spore exines) that have contributed to the coal and trace their effect on the composition and characters of the coal; (2) the nature of the processes, biochemical or chemical, by which the plant cells have been reduced to their present condition.

Why has the structure been preserved in certain cases and disappeared in others? Where contents are observed in the cells are these the original contents (resins, etc.) or were the walls thickened in life (sclerenchyma) or is the filling post mortem? How far are we dealing with the original

[3] Monograph on the Constitution of Coal. London, 1918, H. M. Stationery Office.

cell substances and their contents or to what extent, if any, is coal a "replacement phenomenon" as suggested by Hickling, and the structure pseudomorphic? Why are some cells "fusainized" and others not? These questions must be regarded, so far as British coals are concerned, as largely unsettled.

My efforts, up to the present, have been chiefly devoted to the interpretation of the structures found, that is to say, the problem of inferring from them the kind of cell or of tissue that they represent. I give here some examples of the way in which the cell, in general, may be degraded in Welsh coals.

Fragmented Cells

Cellular fragments of a characteristic shape and disposition are frequently found, chiefly in fusain lenticles, but also embedded in bright coal and passing into it; these are shown in Fig. 1. The fragments are bounded by arcs, or bows, and the linear arrangement is sometimes, as in this case, well marked. Such fragments are familiar to the petrologist, and structure of this kind is called by Mugge's term "bogen" structure, that is arc structure. The structure is highly characteristic of comminuted vesicular or cellular rocks, such as lava, tuffs of basalt, etc.

The obvious interpretation is that the structure represents fractured secondary tissue, which might be either xylem or cortex. This interpretation has, however, been disputed, and the fragments called "algal cells," so that it is important to be certain of the interpretation. The steps which prove that it really is fractured secondary tissue may be seen in the following illustrations.

Fig. 2 shows bogen structure in anthracite. In Fig. 3, there is a similar "bogen" structure, with the peculiarity of one or two dots in nearly every fragment. The interpretation is given, by Fig. 4, from an adjoining portion of the same coal; this shows that the dots are the intercellular spaces left, as is common in certain plant tissues, at the angles where cells touch each other. Complete hexagonal cells may be seen amid the fragments. The same thing is shown in Fig. 5 from a different Welsh anthracite. In Fig. 2, close inspection will reveal faint lines extending from the angles of the fragments and meeting near the center. Prolonged etching, as in Fig 6, brings them out more clearly; Turner's method also shows them. Their interpretation is made clear by Fig. 7, which is from a Scotch anthracite. Here the intercellular spaces are joined by dark lines, which clearly represent the middle lamellæ of the cells. That the cells were elongated is proved by Fig. 8, which shows them cut obliquely with the middle lamellæ quite distinct.

That the cells were those of secondary tissue, either xylem (wood) or periderm (cork) is thus certain, but there is no evidence to prove which.

Periderm, in which the cells were disposed in lines, was well developed in most of the coal plants. In some cases of bogen structure, there is an

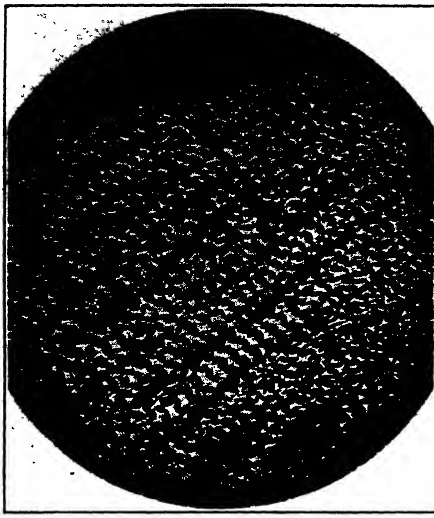


Fig. 1.—Bogen structure in anthracite; etched with Schulze's solution. × 100.

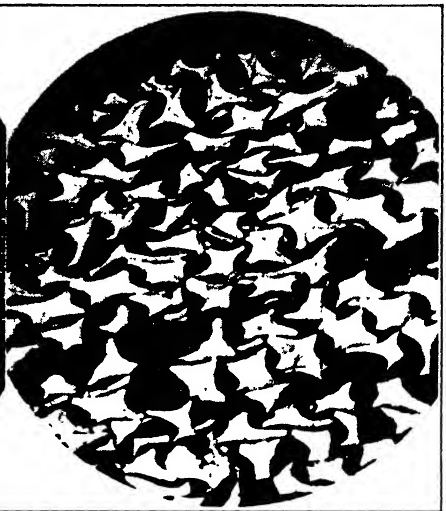


Fig. 2.—Bogen structure in anthracite; chromic etched. × 450.

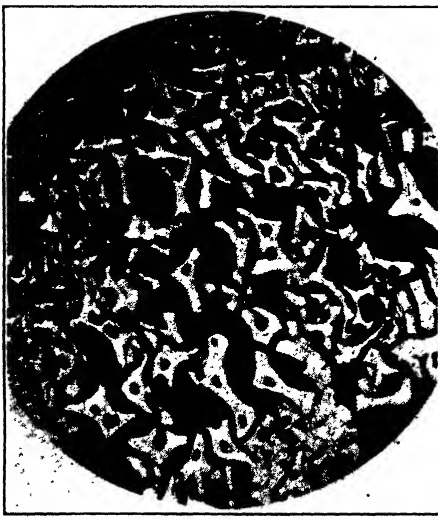


Fig. 3.—Bogen structure in anthracite; chromic etched. ×450.

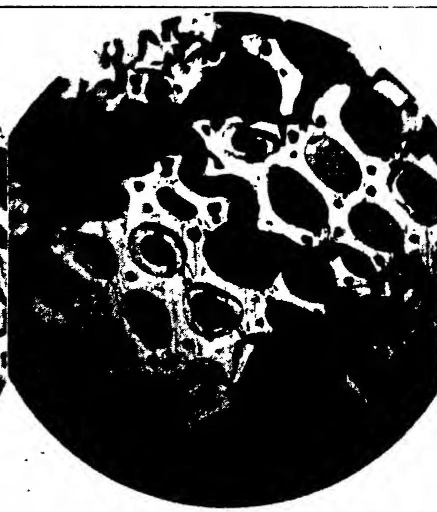
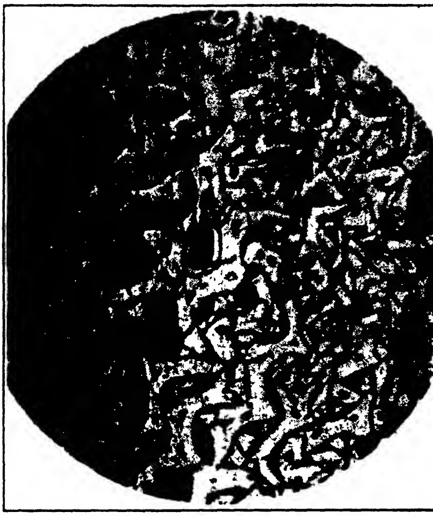


Fig. 4.—Complete cells, showing intercellular spaces, same sample as in Fig. 3; chromic etched. × 450.

indication of medullary rays, which would prove it to be wood. In others, this evidence (or that of pitted tracheids) is absent and it is possible that the persistent occurrence of well-marked intercellular

spaces, as in Figs. 5 and 4, may indicate cortical tissue. This is a point that I hope to investigate further.



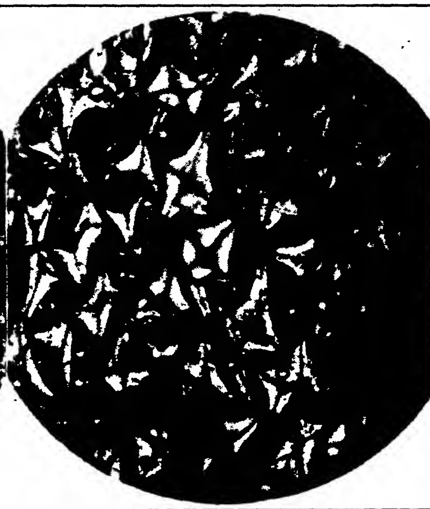


FIG. 5.—BOGEN STRUCTURE AND COMPLETE CELL IN WELSH ANTHRACITE; CHROMIC ETCHED. × 450.

FIG. 6.—BOGEN STRUCTURE, SHOWING MIDDLE LAMELLÆ; CHROMIC ETCHED. × 450.

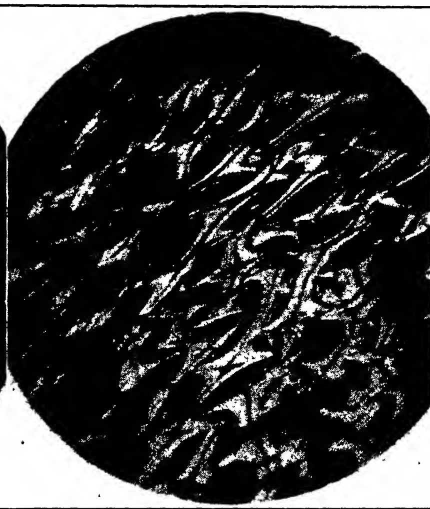


FIG. 7.—CELLS UNCOMPRESSED AND COMPRESSED IN SCOTCH ANTHRACITE; FLAME ETCHED. × 450.

FIG. 8.—ELONGATED BOGEN STRUCTURE IN WELSH ANTHRACITE; FLAME ETCHED. × 450.

UNFRAGMENTED CELLS

Bogen structure may be seen passing into coal in which the cells are unfractured, as in Fig. 9 (Welsh anthracite). In Fig. 10, the bogen

structure has given place to unfractured cells linearly disposed. In this case, the lumens of the cells are greatly reduced. Whether this

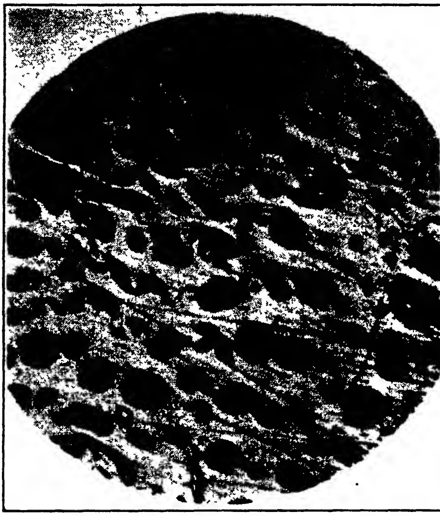


FIG. 9.—PASSAGE FROM FRACTURED TO UNFRACTURED CELLS IN WELSH ANTHRACITE; CHROMIC ETCHED. × 450.

FIG. 10.—UNFRACTURED CELLS IN WELSH ANTHRACITE; CHROMIC ETCHED. × 450.

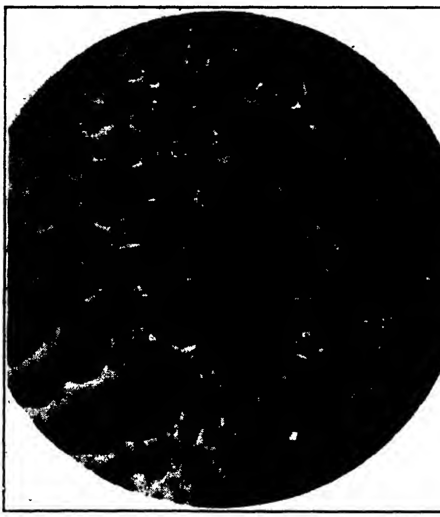


FIG. 11.—CELLS SHOWING INTERCELLULAR SPACES AND MIDDLE LAMELLÆ IN SCOTCH ANTHRACITE; FLAME ETCHED. × 450.

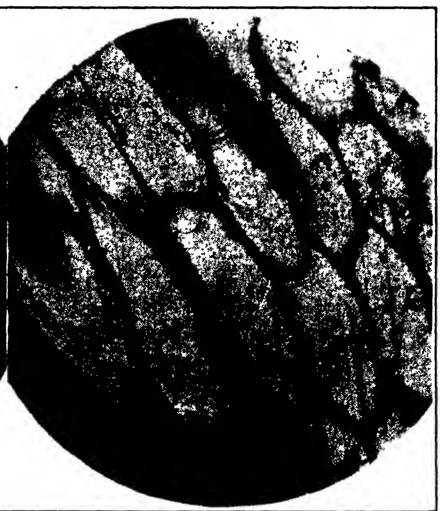


FIG. 12.—COMPLETE CELLS IN WELSH ANTHRACITE; FLAME ETCHED. × 450.

represents a fragment of sclerenchyma in which the walls were so thickened as to reduce the lumens to mere points, or whether the cells have

been filled post mortem by a colloidal substance which became bright coal, is an important but unsettled point. In this case, there are no

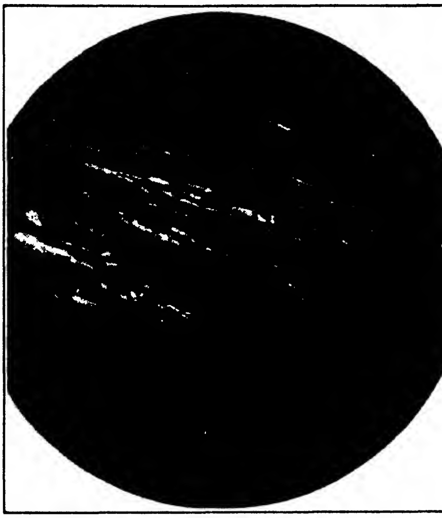


FIG. 13.—WELSH ANTHRACITE; FLAME ETCHED. × 450.

FIG. 14.—WELSH ANTHRACITE; FLAME ETCHED. × 450.

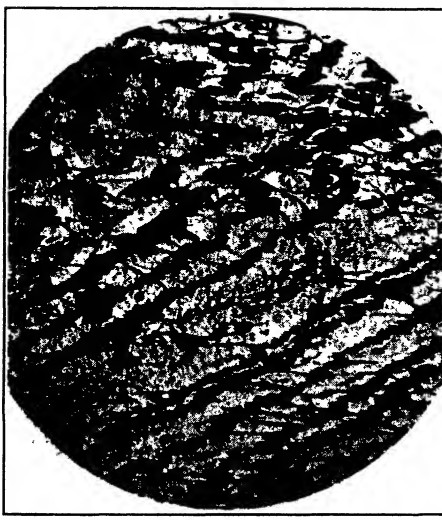


FIG. 15.—MEDULLARY RAYS AND WOODY TISSUE IN CROSS-SECTION FROM FOSSIL STEM; CHROMIC ETCHED. × 100.

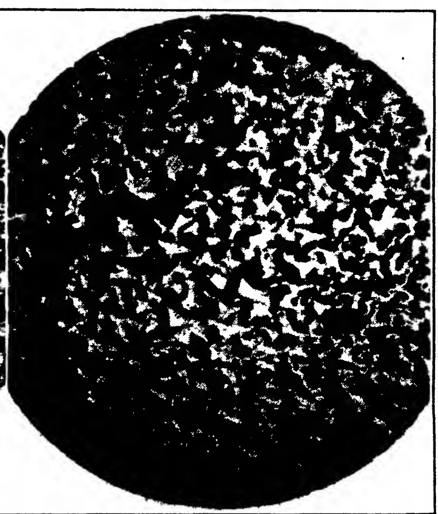


FIG. 16.—WOODY TISSUE AND MEDULLARY RAYS IN CROSS-SECTION OF FOSSIL STEM; CHROMIC ETCHED. × 450.

middle lamellæ to be seen, nor did flame etching reveal them. It looks as though the middle lamellæ had early decayed. When they were filled by a dark matrix, they are easily seen on etching and may be

the most persistent feature in the survival of the cell. In other cases, they have been filled with bright coal or compressed in a plastic state and vanished.

The same applies to the lumens. Where they have been filled with a dark matrix they survive. When fractured, the juxtaposition of the arcs of the fragments form highly characteristic figures, consisting of alternate lenticular spaces joined by curved lines. Such spaces may be seen in Figs. 5 and 9. They often occur in a mass of structureless coal and may be the only survival of structure, but they may be sufficient to show that we are dealing with what was once secondary xylem or cortex

FIG. 17.—WOODY TISSUE IN LONGITUDINAL SECTION OF FOSSIL STEM, SHOWING TRACHEIDS WITH BORDERED PITS; CHROMIC ETCHED. × 450.

FIG. 18.—SPORES IN CROSS-SECTION OF WELSH ANTHRACITE (DULL COAL); ETCHED WITH SCHULZE'S SOLUTION. × 50.

In other cases, the lumen may disappear, either by compression or filling with a bright coal-matrix, and the middle lamellæ alone survive as dark lines. If intercellular spaces are present they may survive as dots, or we may have a series of lines and dots; this may be observed in Figs. 7 and 11. The compression has closed the lumens and reduced them to faint lines, while the middle lamellæ and intercellular spaces remain as parallel lines with dots at regular intervals.

Occasionally the cell structure is extremely well preserved, as in Fig. 12. The cell walls may be seen on close inspection to be perforated, and I think we have here an oblique section of scalariform tracheids.

From the question of the survival of cells in general, we pass to the question of the identification of tissues. Of these the most important

is woody tissue. To identify this we have to rely on three characteristics: (1) the occurrence of pitted tracheids, (2) the presence of medullary rays running at right angles to the tracheids and often containing resin, and (3) the presence of wood parenchyma or cells resembling the rays in form and contents, but parallel to the tracheids.

The pitted cells may sometimes be observed in anthracite; Fig. 13 is an example, in Fig. 14 we have the remains of scalariform pits. The medullary rays are often hard to trace, but they seem to survive in some cases as lines, often showing bogen structure.

A very instructive specimen was given me by Doctor Wheeler last July, which we propose jointly to investigate chemically as well as microscopically. It consists of a fossil stem in which the pith has been replaced by shale or stone, around which there is a layer of bright bituminous coal over an inch in thickness. Fig. 15 shows the appearance of a transverse section under a low magnification. The medullary rays are seen as dark lines thrown into waves in some places by compression. A part of the same section magnified 450 diameters is shown in Fig. 16. Note the characteristic "arc and lenticule" spaces left by the displaced fragments of the large cells of the medullary rays. A longitudinal section, magnified 450 diameters, is shown in Fig. 17. In this, the long tracheids are seen with what, I think, are clearly "bordered pits," such as are found in coniferous wood. The large cells of the rays are cut transversely.

The characteristics of cortical tissue are not so clearly made out, but cortex can certainly give rise to bright coal. I have some flattened stems of sigillaria and lepidodendron with a very thin bright coaly layer marked by the leaf bases and scars. I have succeeded in polishing and etching these and showing the cellular structure in places. The cells have large intercellular spaces and middle lamellæ, but are not filled with a dark matrix, and are difficult to photograph. So in anthracite showing marks of the bark of lepidodendron I have observed nearly complete cells, with lumens and intercellular spaces joined by middle lamellæ. The further investigation, it is hoped, will throw light on the characters of bright coal formed from cortical tissues and not from wood.

A word may be said concerning the dull coal. It contains comminuted fragments of all sorts of tissue. Spore exines are frequently but not always present. Megaspores in anthracite are shown in Fig. 18. Dull coal, however, appears to exist in very small quantity in Welsh anthracite. When it occurs, it is often called "anthracite cannel" or pitch-like coal, but it resembles cannel only in appearance. If Thiessen is correct in attributing bright coal to larger fragments of wood (or perhaps one should say if this should be true of British coals) it has evidently an important bearing on the origin of anthracite. I have forborne to discuss this question or indeed to attempt to make any

generalizations until more data have been accumulated by the systematic examination of the British coal fields. I have made a beginning of such a study of the Welsh coal fields, but an enormous amount of work remains to be done. The method of etching by reagents, however, has, I think, established itself as a powerful instrument for the microscopic investigation of coal.

Microscopical Structure of Anthracite

By Homer G. Turner,* Bethlehem, Pa.

(New York Meeting, February, 1925)

Coals, other than anthracite, have been so thoroughly studied under the microscope during recent years, that we now know what kinds of plants and what parts of plants form the bulk of lower rank coals from peat to bituminous coal. The microscope has also shown the state of preservation of such vegetation as well as the nature and distribution of products of plant decay. These and further details have been ascertained mainly through the employment of two methods of attack, section cutting and maceration.

Anthracite has failed to respond to these methods, so well adapted to the study of lower rank coals and, therefore, has been neglected by investigators to such an extent that there is much doubt as to its microscopical characteristics. The object of this paper is to lift anthracite from its realm of obscurity by demonstrating the wealth of microscopical detail that is revealed when reflected light is used on a properly polished and etched surface and, further, to show the relationship between anthracite and bituminous coal.

Technique

The method adopted in this investigation is similar to that described in an earlier paper.[1] Because of slight modifications recently made, the process is again described. It consists, briefly, of etching a polished surface of coal with heat. Although pieces of various sizes and shapes are used, blocks of coal about 2 or 3 cm. square take the most uniform polish and are large enough to be handled with ease. Larger pieces can be used if one has the equipment for polishing them and they may be desirable when one wishes to study some particular form that extends for some distance through the coal. Large surfaces, however, require greater care in polishing and etching; for this reason, they are not recommended for ordinary work.

* Assistant Professor of Geology, Lehigh University.

[1] H. G. Turner and H. R. Randall: A Preliminary Report on the Microscopy of Anthracite Coal. *Jnl. of Geol.* (1923) **31**, 306.

Small blocks are cut from the coal by means of an ordinary hacksaw. Two surfaces, one parallel to the bedding and one at right angles to it, are ground to planes. All sharp edges are beveled slightly to prevent pieces from breaking off and scratching during the subsequent smoothing. These plane surfaces are then polished to remove saw marks and scratches.

The methods commonly used in polishing metals may be employed. The object is to obtain a scratchless surface with the minimum of time and effort. The method that yields best results consists of first grinding on a revolving iron lap with medium-sized carborundum powder and water; next grinding by hand on plate glass, using a paste of flour alundum and water; and then polishing by rubbing upon a piece of fine canvas or similar cloth stretched on a flat block, using again a paste of flour alundum and water. The final buffing is done by rubbing the washed and dried specimen on broadcloth with diamantine, or on wet broadcloth with magnesium oxide. All rubbing is done in a circular path, with the exception of the final few motions at each stage; these should be in one direction so one can tell when all the scratches produced by one rubbing are removed by the next. The polished surface thus produced may not be free from scratches, but these will not be objectionable if the final buffing has been done in one direction so that the scratches are easily recognized by their position. On laminated surfaces, the final polishing and buffing should be across the layers and not parallel to them.

The specimen is placed in a drying oven over a Bunsen burner and heated from room temperature to about 220° C., to remove moisture and to obviate splitting of the surface as the result of sudden heating during the etching process. After this temperature has been maintained for about an hour, the specimen is removed with warm forceps and the polished surface immediately brought to a red heat by applying the oxidizing blowpipe flame at right angles to the face. A differential oxidation is thus produced, which reveals the structure without destroying the polish.

Different coals and different layers in the same coal may etch at different rates, making it necessary at times to warm and etch repeatedly to bring out the greatest detail. If the coal splits badly when being etched, it must be immersed in clean dry sand with only the polished surface exposed, heated to about 300° C., and etched in place using a blast lamp.

The etched coal is studied with the metallographic microscope, using vertical illumination from a carbon arc. A good working objective is one giving a magnification of from 150 to 200 diameters.

Banding of Coal

All ordinary anthracite, on close examination, is found to be more or less laminated and composed of layers differing from one another in color, luster, texture, mode of fracture, and thickness; Fig. 1. In general,

brilliant jet-black layers alternate with bright black or gray bands, in which are embedded thin sheets of dull material resembling charcoal. The brilliant layers consist of lenticular masses embedded in the bright gray to black coal. They vary in thickness from a few microns to a centimeter or more, and correspond to the layers in bituminous coal that

FIG. 1.—JOINT FACE OF ANTHRACITE, OF PENNSYLVANIA AGE, FROM THE ANTHRACITE REGIONS OF PENNSYLVANIA. LUMP SHOWS SEVERAL FLATTENED JETLIKE STEMS, APPEARING ON FACE OF COAL AS BRILLIANT BLACK BANDS; THESE BRILLIANT BANDS *a*, AS WELL AS DULLER PORTIONS *b*, IN WHICH CAN BE SEEN FINE LAMINATIONS, ARE IN ENTIRE AGREEMENT WITH ORDINARY BITUMINOUS COAL. NATURAL SIZE.

have been called, by various authors, "bright coal," "glanz," and "anthraxylon." The bright bands are thicker than the brilliant jet-black ones, although, on close inspection, they are shown to contain many thin sheets of the brilliant black coal and thin sheets of dull material. These bright bands correspond to the layers in bituminous coal that have been termed "dull coal," "mat," and "attritus,"

The brilliant layers are more compact than the duller ones and possess a more perfect conchoidal fracture. Where they are thick, the broken surface often shows rounded or oval fracture forms. Some varieties of anthracite appear, at first glance, to be composed wholly of the brilliant coal, revealing their various laminæ only on careful examination. Other

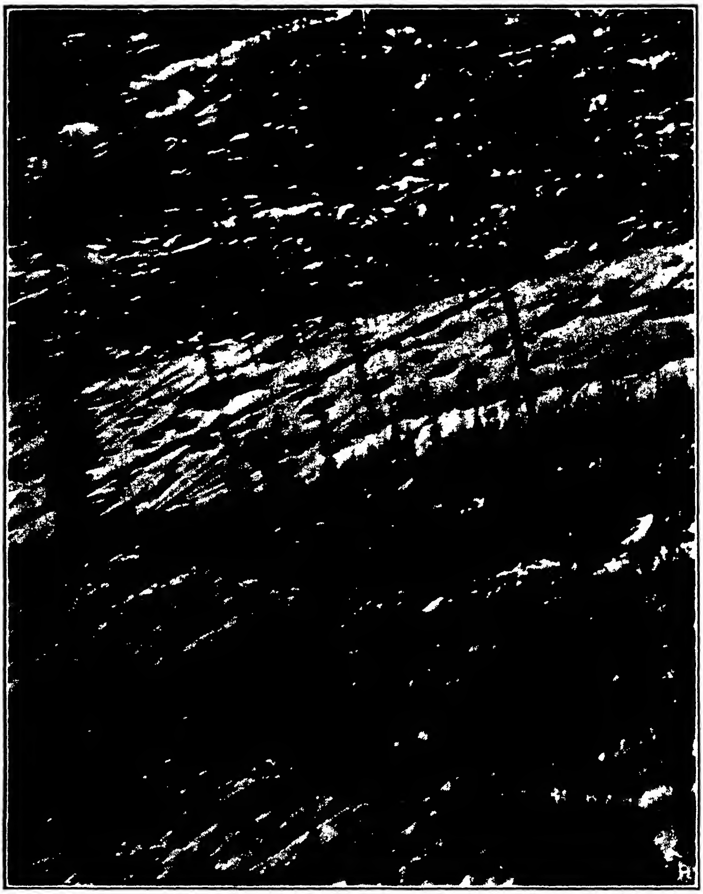


FIG. 2.—FRAGMENT OF WOOD EMBEDDED IN GRANULAR MASS OF DEBRIS COMPOSED OF MUD, MACERATED PLANT MATTER, AND FRAGMENTS OF MANY KINDS OF PLANT MATERIAL; HIGHLY COMPRESSED CONDITION OF THE WOOD IS SHOWN; SHARP CRACK ACROSS WOOD SHOWS BRITTLE CONDITION OBTAINED BEFORE HARDENING OF DEBRIS WHICH FILLS THE CRACK. FROM BED NO. 5, CAMERON COLLIERY, SHAMOKIN, PA. × 140.

varieties seem to be composed largely of the bright material, in which are embedded only occasional lenses of brilliant coal.

Mineral charcoal is abundant in almost all anthracite. Cleaving coal parallel to the banding exposes charcoal-covered surfaces in every specimen that shows distinct lamination. In fact, it is almost impossible to

find a square inch of laminated coal that does not show charcoal either in thin sheets or lenses. On the other hand, the varieties that are poorly laminated and almost uniform in luster contain little charcoal. The absence of distinct lamination is no doubt due, in part, to the paucity

FIG. 3.—WIDE PIECE OF WOOD SHOWING, IN ONE PORTION *a*, FLATTENING TO SUCH AN EXTENT THAT THE WOOD STRUCTURE IS ALMOST OBLITERATED, WHILE PRESERVING WOOD STRUCTURE IN ANOTHER PORTION *b*, ALTHOUGH THE FIBERS HERE ARE HIGHLY COMPRESSED. FROM LOWER PART OF BED NO. 5, CAMERON COLLIERY, SHAMOKIN, PA. × 140.

of dull charcoal. In addition to the thin sheets of charcoal so commonly found in the bedding planes, one finds occasional charcoal lenses several inches in thickness, composed of crisscrossing chips 2 cm. or more in length and 1 cm. in width. Detached chips of these dimensions are also encountered with the coal bands warping around them.

The above megascopic description of anthracite, aside from the luster which is on the whole much brighter, applies equally well to bituminous

coal. In fact, it would be difficult to distinguish between anthracite from Pennsylvania and bituminous coal from Illinois were it not for the difference in luster.

The bright layers in bituminous coal have been shown, by the microscope, to consist of wood fragments of various kinds in varying states of

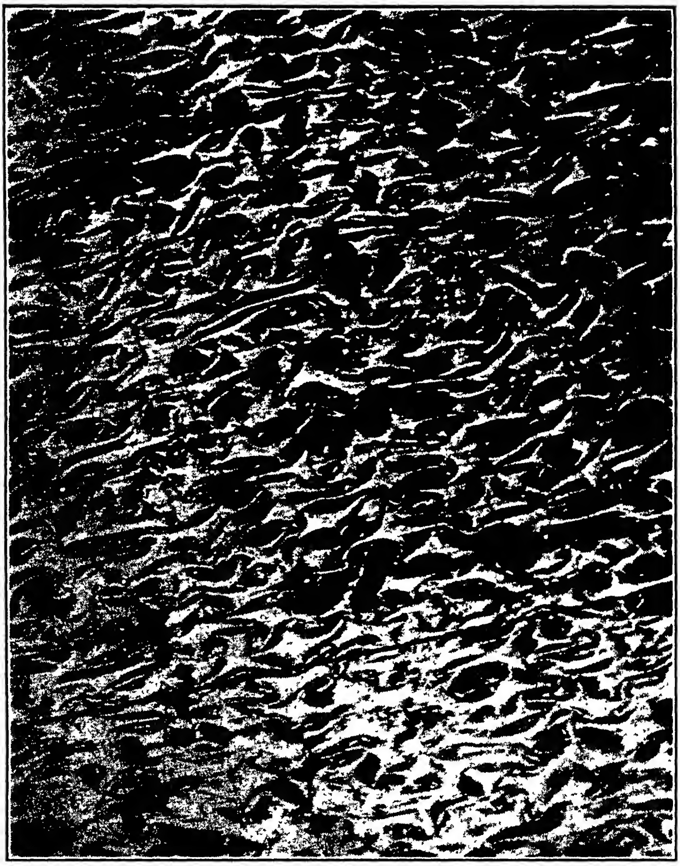


FIG. 4.—CROSS-SECTION OF WOOD APPEARING AS A BRILLIANT BAND IN THE COAL; WALLS OF WOOD FIBERS HAVE BEEN FOLDED AND COLLAPSED ALTHOUGH NOT GREATLY FRACTURED; WHOLE SECTION APPEARS BRILLIANT UNDER MICROSCOPE SHOWING NO BLACK DULL MATTER, SUCH AS IS SEEN IN FIG. 5. FROM LOWER PART OF BED NO. 5 CAMERON COLLIERY, SHAMOKIN, PA. × 140.

preservation. The duller layers of bituminous coal are likewise shown to consist of a mass of finely macerated plant matter containing many kinds of tissues, plant cells, fibers, cuticles, resinous matter, pollen grains, spores, and mineral matter. In this mass of debris are also found small bright lenses of woody matter with sheets and chips of dull mineral charcoal. To show the true relationship between anthracite and bituminous

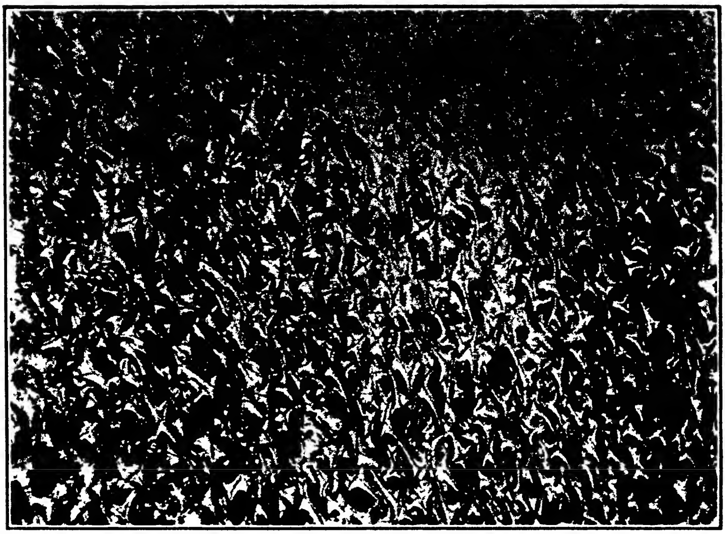


FIG. 5.—CROSS-SECTION OF WOOD SHOWING FRACTURED, SOMEWHAT BENT, AND TELESCOPED CELLS WITH SOME BLACK LUSTERLESS MATERIAL AROUND CELL FRAGMENTS; BRITTLENESS AND PRESENCE OF DULL BLACK MATERIAL SUGGESTS CRUSHED CHARCOAL, ALTHOUGH AS IN FIG. 2, THE BRILLIANT WOODY FRAGMENTS HAVE BECOME BRITTLE BEFORE WHOLE COAL MASS WAS HARDENED; MANY FRAGMENTS OF THIS NATURE ARE FOUND IN ANTHRACITE. FROM CAMERON COLLIERY, SHAMOKIN, PA. × 235.

FIG. 6.—SOMEWHAT OBLIQUE CROSS-SECTION OF WOOD FROM A SMALL STRIP OF BRILLIANT COAL; CELLS ARE SO WELL PRESERVED AND SO LITTLE FLATTENED THAT IT SUGGESTS CARBONIZED WOOD MADE DENSE BY AN INFILTRATION OF PUTRIFICATION PRODUCT SOLUTIONS. FROM FORGE SPLIT OF THE MAMMOTH BED, NANTICOKE, PA. × 235.

coal, it is necessary, therefore, to reveal the microscopical characteristics of those components of anthracite that are so obviously duplicated megascopically in bituminous coal.

Brilliant Layers, or "Anthraxylon"

The brilliant layers of anthracite, when examined under the microscope, are found to be derived from pieces of wood, such as limbs, stems,

Fig. 7.—Part of Fig. 6 showing great detail revealed by method of treatment described in this paper; note the delicate dumbbell-shaped membrane within cells and elliptic markings surrounding small knots along cell walls. × 1000.

twigs, and roots. Wood structure has been preserved in many of them, although it is absolutely lacking in the majority. The cells range from almost perfect forms to forms that have been greatly flattened. Most of the bands seem to have been greatly compressed. In Fig. 2 is shown

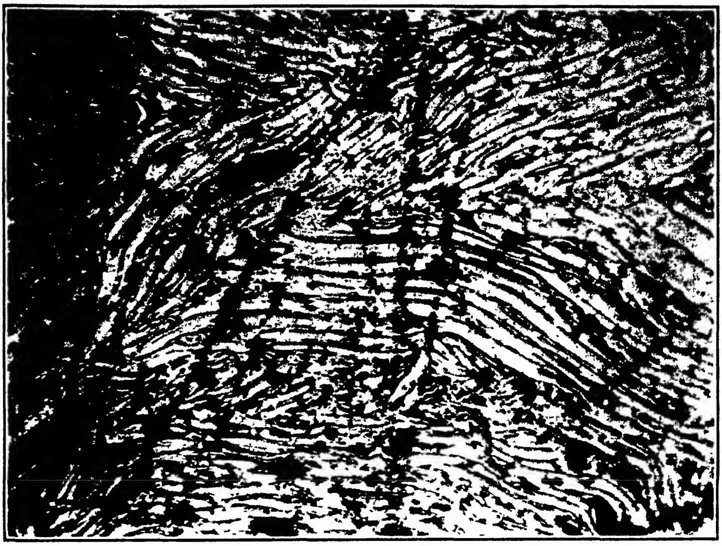


FIG. 8.—A SECTION CROSSWISE TO BEDDING SHOWING PLICATED BUT LITTLE FLATTENED WOOD FIBER; THIS AGAIN MAY REPRESENT DENSIFIED CHARCOAL. FROM PRIMROSE BED, WILLIAM PENN COLLIERY, PA. × 235.

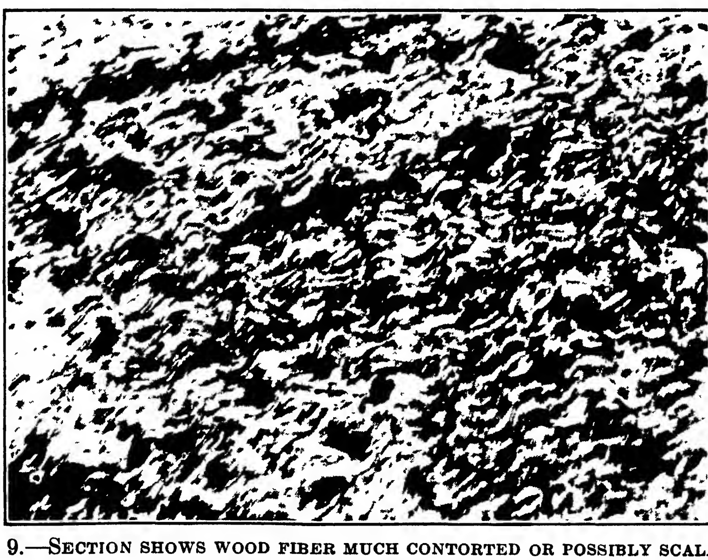


FIG. 9.—SECTION SHOWS WOOD FIBER MUCH CONTORTED OR POSSIBLY SCALARIFORM MATERIAL; PERFECT PRESERVATION SHOWN AGAIN SUGGESTS HARD CARBONIZED MATERIAL. FROM PRIMROSE BED, WILLIAM PENN COLLIERY, PA. × 235.

a typical brilliant band, greatly compressed yet showing distinct wood texture. A break in the strip shows that this piece of wood became brittle before the ground mass in which it was embedded. Fig. 3 is a broad brilliant band that shows the transition from well-defined wood texture to almost structureless material. This photograph is of partic-

FIG. 10.—A LARGE, WRINKLED SPORE EXINE FOUND IN DULLER LAYERS OF ANTHRACITE FROM PENNSYLVANIA. × 235.

ular importance for it shows that the woody matter may be so flattened that it appears homogeneous. Most of the structureless bands will show wood grain on their sides or ends if examined throughout their length and width. It seems logical, therefore, to assume that the brilliant bands which are absolutely structureless are the result of extreme compression. Such structureless bands are not uncommon in certain English bituminous coals, where they have been named "vitrain." Fig. 4 shows a condition sometimes met, where the cells have been crushed and folded. Figs. 2 to 4, then, show the usual appearance of the brilli ant

bands, making clear also why some of the bands seem structureless because of great compression.

The brilliant bands in Figs. 6 to 9 show such perfect structure that they suggest pieces of wood which were not as plastic as the average. These fragments may represent partly carbonized wood or carbonized

Fig. 11.—Large spore exines from duller layers of coal; markings on the spores are probably lines of dehiscence. Found in Pennsylvania anthracite. × 300.

wood that has been thoroughly impregnated with the putrification-product solutions during subsequent immersion in the bog.

As in bituminous coal, the woody matter forms the largest part of the deposit. Aside from the pronounced woody lenses mentioned, small chips, single cells, small groups of cells, and other woody products are found in the mass of debris designated here as bright coal.

Bright Coal, or "Attritus"

This material is a complex granular ground mass, composed of a great number of constituents derived from various parts of plants

together with mineral grains and substance with the appearance of mud. Some of the easily recognized things embedded in this ground mass are spores, megaspores, cuticles, former resinous matter, pith, plant fibers, plant cells and parts of cells, finely macerated woody matter, and mineral grains; Figs. 10, 11, and 12 show the types of megaspores observed. A

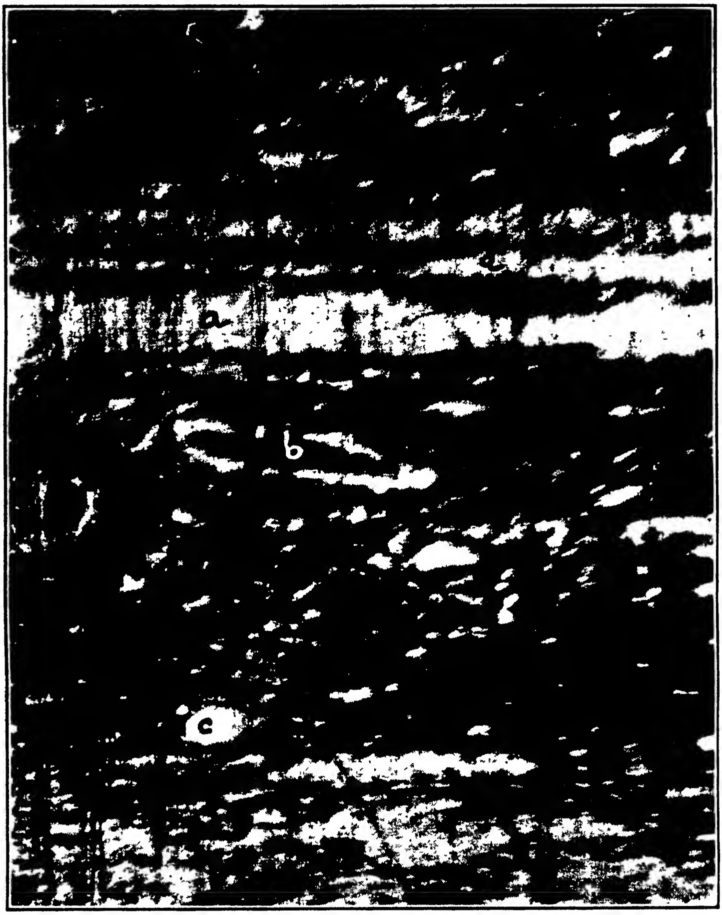


FIG. 12.—VIEW OF THE GROUND MASS SHOWING *a* STRIPS OF BRILLIANT STRUCTURELESS WOOD, *b* LARGE SPORE EXINE, *c* FORMER RESIN BODY, AND SMALL FRAGMENTS OF PLANT DEBRIS INCLUDING MICROSPORES. FROM BED NO. 5, CAMERON COLLIERY, SHAMOKIN, PA. × 140.

macerated fragment of wood containing round resin bodies is shown in Fig. 13. In Fig. 14 is shown a longitudinal section of the primary wood of a lepidodendrid surrounded by plant fragments of various kinds. Fig. 17 shows carbonized groups of vascular bundles surrounded by cuticles and strips of wood showing good cell structure, although greatly flattened.

All these forms, and many others too small to show in the photographs, but clearly visible under the microscope, have their counterparts in the corresponding bands of bituminous coal.

Dull Layers—Carbonized Matter

The carbonized matter of coal has been called "charcoal," "mother of coal," and "fusain." That there is a great amount in anthracite is

Fig. 13.—Section crosswise to bedding; this section through the duller layers shows a somewhat macerated wood fragment containing round bodies which are probably vessels formerly filled with resin or gum. From Primrose bed, William Penn Colliery, Pa. × 235.

indicated by the foregoing megascopic description. This material varies in hardness and texture and, possibly, in composition. Most of it shows good plant structure, being structureless in rare cases only. Figs. 18 and 19 represent cross-sections of large fragments of material that, to the unaided eye, look like fragments of ordinary charcoal. One piece (Fig. 18) is so soft that it crumbles readily in the fingers; the

thin walls of the perfect cells show the reason for this behavior. The other piece (Fig. 19) is so hard that it can just be scratched with the finger nail. The reason for this superior hardness is shown in the much thicker cell walls and component bright bands of hard coal material. In both of these fragments the cells are devoid of filling. Fragments of other charcoal-like material were isolated and found to be too hard to be scratched with the nail. Under the microscope, these hard fragments

FIG. 14.—A SECTION THROUGH THE DULLER LAYERS SHOWING A LONGITUDINAL SECTION OF PRIMARY WOOD OF A LEPIDODENDRID a; NOTE DELICATE SCALARIFORM STRUCTURE. FROM BED NO. 5, CAMERON COLLIERY, SHAMOKIN, PA. × 140.

show crushed and fractured cells, as illustrated in Fig. 5. It is suggested that this particular material represents carbonized wood which had been densified by infiltration of products of vegetal decay and further hardened by compression. It can be seen that in the bright coal (Fig. 4) the cells are warped and crushed, while in Fig. 5 they are crushed and fractured. In the duller portions of the coal, carbonized fragments are also found having perfect cell structure, with the cells filled with dull structureless material; these are represented by Figs. 20 and 21.

The charcoal-like materials are similar in that they show almost perfect structures. This would suggest that they escaped the jelly stage of the other materials in the bog. Difference in thickness of cell walls and of cell filling may indicate differences either in stages of carbonization or oxidation before burial, or in original composition, or in behavior after burial.

Conclusions

It is evident, from the foregoing, that anthracite responds readily to the method of treatment herein described. The photographs show that very delicate microscopical details are made clearly visible. It has been shown further that anthracite is composed of the same kinds of organisms

FIG. 15.—STRIPS OF BRILLIANT STRUCTURELESS WOOD *a*, FLATTENED CELLS *b*, WARPED AND FRACTURED CELLS *c*, AND FIBERS OF PRIMARY WOOD OF A LEPIDODENDRID *d*. FROM BED NO. 5, CAMERON COLLIERY, SHAMOKIN, PA.

and materials found in bituminous coal; that these organisms and their parts are in the same proportions as they are in bituminous coal; and also that these organisms are in a similar state of preservation, except for the greater abundance of structureless bands produced by intense flattening of wood components.

DISCUSSION

E. S. Moore,* Toronto, Ont.—These papers should end the difficulties some people have in accepting the opinions of most geologists that there is really no difference between bituminous coal and anthracite in nature of deposition and physical constitution. The suggestion that

Fig. 16.—Probably a transverse view of primary woody tissues of a species of Lepidodendron showing scalariform structure; note unusually thick cell walls, giving the appearance of fruit stone structure. From Pennsylvania anthracite.

the anthracite of Wales is different from that of America seems to indicate that some of the Welsh scientists are loath to give up the idea that the origin of the Welsh anthracite cannot be explained, as we explain it in America, by influence of pressure. I would like to ask if the author has found any marked difference in the spore content, so far as his studies have gone between the Pennsylvania anthracite and the Pennsylvania

* Professor of Economic Geology, University of Toronto.

bituminous coal, and also whether in the attempt to apply this microscopical study in the correlation of the anthracite seams, his efforts have met with much practical success.

EDWARD C. JEFFREY, Cambridge,* Mass.—There is a distinctive value in having more than one method of studying anthracite. Etching, whether effected by chemicals or by flame, is a much more rapid method

FIG. 17.—VASCULAR BUNDLES *a* SURROUNDED BY LEAF CUTICLE *b* WITH COMPRESSED WOODY FRAGMENTS *c* BORDERING THE WHOLE. SPECIMEN FROM FORGE SPLIT OF MAMMOTH BED, NANTICOKE, PA. × 100.

for getting results, but the thin sections will give a clearer idea of the organization of anthracite.

REINHARDT THIESSEN,† Pittsburgh, Pa.—Doctor Seyler has proved that beyond any doubt. The idea has been formed that it is very difficult to make thin sections. This is not so difficult; we have made as many as eighteen thin sections in a day and if you can make eighteen

* Professor of Botany, Harvard University.

† Research Chemist, Bureau of Mines.

surfaces by his method, you are doing pretty well. It has also been said that it is impossible to make a thin section of brown coals; recently I have made several dozen thin sections of brown coals.

H. J. Rose, Pittsburgh, Pa.—It is very easy to find mother-of-coal structure in metallurgical coke; a single cut section may show ten or twenty fragments.

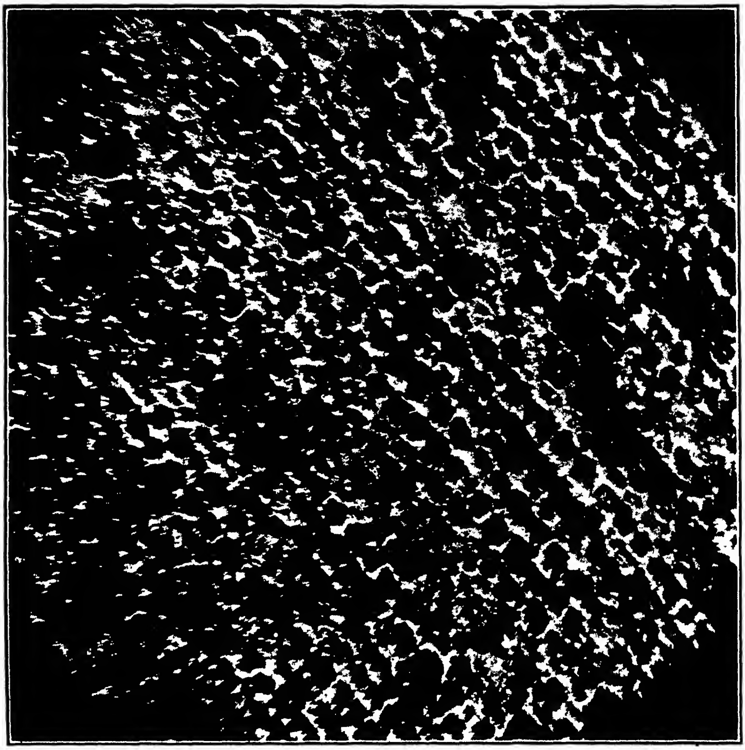


Fig. 18.—Isolated fragments of friable charcoal showing simple and perfect cell structure; cell walls are thin and cells empty. Fragment was so fragile that it had to be boiled in balsam and xylol before polishing in regular way; etching was not necessary to bring out structure shown. Compare with Fig. 19. From thick lens in Mammoth bed stripping near Mt. Carmel, Pa. × 120.

James F. Kemp, New York, N. Y.—About ninety years ago, a Professor Bailey, of the Military Academy at West Point, when sitting before his grate fire, noted that a thin film of ash revealed traces of plant structure.

David White, Washington, D. C.—The methods of sectioning carbonized vegetable debris for microscopical study, brought to such perfection by Doctors Jeffrey and Thiessen, open the way to the investigation of the morphology of a wealth of carbonized or coalified plant remains

previously baffling the student. They should lead to great discoveries in the mutual relations and evolution of the plants of all periods. The revelation in microscopical detail of the morphological secrets of the anthracites is now made possible through the modes of treatment developed by Seyler, Turner, and others.

CLARENCE A. SEYLER, Swansea, Wales (written discussion).—A comparison of the results obtained by the author for American anthracites with those obtained by me for Welsh anthracites (partly by his

FIG 19.—ISOLATED FRAGMENT OF CHARCOAL SHOWING ALMOST PERFECT CELL STRUCTURE WITH THICKER CELL WALLS THAN SHOWN IN FIG. 18. THIS PIECE WAS HARD ENOUGH TO TAKE A GOOD POLISH WITHOUT BOILING IN BALSAM MIXTURE; CELLS ARE EMPTY AND STRENGTHENED HERE AND THERE BY BANDS OF BRILLIANT STRUCTURELESS COAL *a*; NO ETCHING WAS APPLIED TO THIS SPECIMEN. FROM CAMERON COLLIERY SHAMOKIN, PA. × 140.

method and partly by that of etching with chromic acid) shows a close similarity between them. Figs. 4, 5, and 9 show fragmented cells ("bogen structure") similar to those illustrated in my Figs. 1 to 6, and his interpretation of them as fragmented woody tissues agrees with mine.[2]

[2] The Microstructure of Coal; see p. 117.

Figs. 6 and 7 show what the author describes as "delicate dumbbell-shaped membranes within the cells and elliptic markings surrounding small knots along the cell walls." Comparison with my Figs. 11 and 12 will show, I think, that the elliptic markings are the intercellular spaces and the knots deposits of pyrites or other extraneous matter within them.

FIG. 20.—CARBONIZED WOOD SHOWING ORIGINAL CELL LAMINÆ. REMARKABLE PRESERVATION MAY BE DUE, IN PART, TO SILICEOUS FILLING SHOWN BY GRAY AREAS WITHIN CELL WALLS, ALTHOUGH SOME CELLS ARE FILLED WITH BLACK, LUSTERLESS CARBONACEOUS MATERIAL; NOTE DELICATE INTERCELLULAR SPACES. FROM FORGE SPLIT OF MAMMOTH BED, NANTICOKE, PA.

The double perforated lines joining the intercellular spaces are the outlines of the middle lamellae, as in my Fig. 12. The dumbbell-shaped spaces are the remains of the lumens, squeezed in the center, the cell walls being either very thick or partly filled with a gelatinized matrix, which has subsequently become bright coal. Fig. 21 may be compared with

my Figs. 7 and 11. The middle lamellae, and intercellular spaces of the uncompressed cells are clearly visible. Supplementary photographs will be found in another publication.[3] While I was in Pittsburgh, Doctor Thiessen gave me some photographs of a German brown coal. The resemblance in every detail to Fig. 11 in the article just above cited, is marvellous.

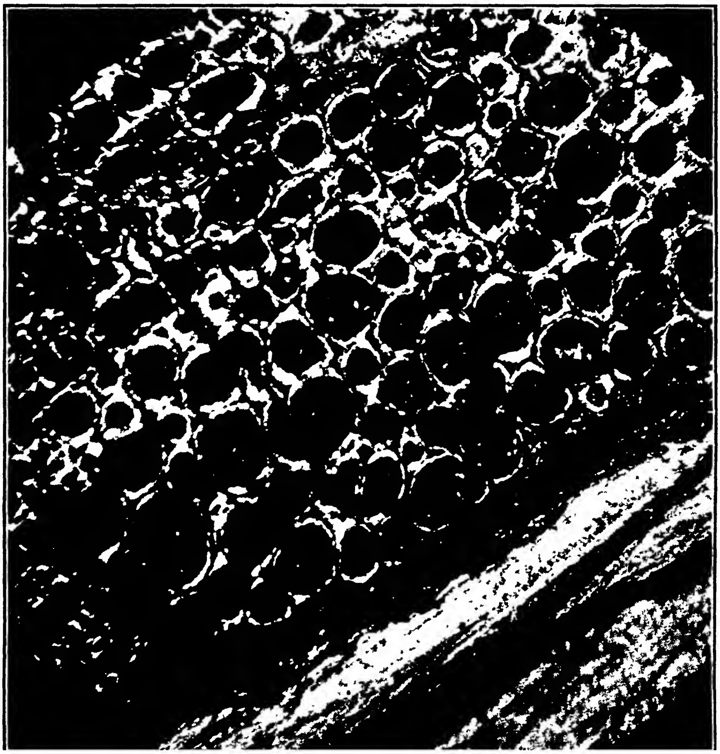


FIG. 21.—CELLS OF XYLEM OR PHLOEM OF A VASCULAR BUNDLE; THIS IS A SECTION THROUGH A DULL CARBONIZED KNOT. SOME CELLS ARE PARTLY FILLED WITH SMALL GRAINS OF PYRITE, WHICH DO NOT SHOW IN PHOTOGRAPH. BLACK CENTERS ARE DULL CARBONACEOUS MATERIAL. FROM FORGE SPLIT OF MAMMOTH BED, NANTICOKE, PA. × 235.

I take this opportunity of acknowledging cordially the great kindness of Doctor Thiessen and all the American coal experts whom I met during my recent visit to the United States and to express on behalf of myself and British colleagues, our pleasure at the opportunity afforded us, by the Institute, of exchanging ideas.

A. C. NOÉ, Chicago, Ill. (written discussion).—Some time ago, the microscopical structure of bituminous coal was thoroughly investigated

[3] Clarence A. Seyler: The Microstructure of Coal. *Fuel in Sci. & Prac.* (1925) **4**, 56.

by Doctor Thiessen. Today, we are presented with a most interesting study of anthracite and it is to be hoped that somebody with equal ability will soon take up the microscopic examination of lignite.

There are a few excellent publications on the microscopy of coal that should be brought to the attention of mining engineers.[4, 5, 6]

The article by Booth[4] shows how the microscopic study of coal pays from a commercial point of view. The author divides coal into three classes, all of which can be quickly determined with the microscope. They are: coals of a woody tissue, which swell considerably on heating and form a very porous coke; coals with a predominance of spore coats and microspores which are practically non-coking; and the non-coking long-flame cannel coals. During the War, new sources of coal in Great Britain had to be tapped and coals were accepted or rejected on microscopical evidence alone; little or no chemical analysis and no large-scale tests were run. This was a great saving of time to the laboratory staffs. Jeffrey[5] has written for the general public that is interested in coal—its origin and its many other aspects. The book contains also much valuable information for the geologist and botanist. It is generously illustrated and can be considered the best popular treatment of the subject in the English language. Potonié's book,[6] written in German, discusses the structure composition and origin of coal for geologists and is the most exhaustive up-to-date handbook on coal petrography.

Professor Turner is the first author who has specialized on anthracite.

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[4] A. L. Booth: The Microstructure of Coal from an Industrial Standpoint. *Jnl.* Royal Microscopic Society of England (June, 1911).

[5] E. C. Jeffrey: Coal and Civilization.

[6] Robert Potonié: Petrography of Coal. Berlin, 1924.

Coal in Relation to Coke

BY EDWARD C. JEFFREY,* CAMBRIDGE, MASS.

(New York Meeting, February, 1925)

THE use of coke in metallurgy, to any important degree, dates from the middle of the 18th century. Its utilization came most opportunely for European civilization. The forests of Europe, except in the most remote and inaccessible regions, had been largely fed, in the form of charcoal, into the smelting furnaces. For a hundred years—the middle of the 17th to the middle of the 18th century—there was a stationary condition of population corresponding to the exhaustion of European forests. This situation, which was particularly evident in Great Britain, was due to the fact that the forests had been depleted and the practical utilization of coke had not begun.

The coking industry is essential for our metallurgical industries, which in turn are basal to healthy economic progress. But coke is of great importance, not only on its own account, but for its byproducts, which enter fundamentally into all the arts of peace and war. The dyestuff industry and the manufacture of explosives are intimately connected with one another, as was shown by the recent war. The subject of coking coal, therefore, is well worthy the serious attention both of practical industry and the scientific investigator.

The most valuable coking coals, from the metallurgical standpoint, are derived from the coals of highest ranks. Coals, for example, that have a carbon ratio of from 70 to 80 per cent. yield the most valuable coke for the blast furnace. The difficulty of investigating these coals, however, is great, for they are rather friable and delicate and possess a high carbon content, which makes them difficult to manipulate. They present, on account of their high carbon content, a considerable degree of opacity when examined, in thin sections, under the microscope. The tenderness of structure and blackness of such high-grade coking coals as those of Connellsville and the Pocahontas region make them extremely difficult to investigate.

Two of my colleagues, who are taking part in this discussion, will describe the valuable results that have been reached by studying coal by the methods of the mineralogist. Doctor White and Doctor Thiessen have studied the structure of coal as determined from thin sections that

* Professor of Botany, Harvard University.

have been polished on the petrographer's grinding lathe. Professor Turner, on the other hand, has investigated the structure of anthracite,

Fig. 1.—Vertical section of oil shale Tasmanite showing presence of numerous flattened spores and of two that have not suffered flattening.

Fig. 2.—Vertical section of a typical cannel coal from Bluegrass, Ky., showing presence of large numbers of spores, a dark matrix, and a lighter colored material, which represents wood now devoid of structure.

the most highly carbonaceous of all carbonic minerals except graphite, by a highly ingenious method of polishing and subsequent etching with

heat. My own investigations have been carried on by still other methods. It has seemed to me that the processes employed, by the biologist, in the study of plants living and extinct, would, with proper modifications, reveal the structure of coal better than any other means. It has taken a number of years of experiment to justify this belief, but the results are

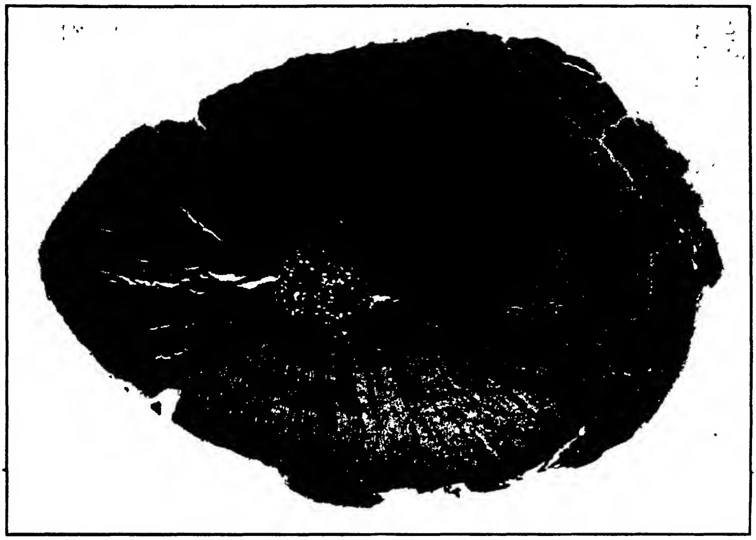

FIG. 3.—END OF A PARTLY CHARRED BRANCH OF A CONIFER FROM THE AMERICAN CRETACEOUS.

FIG. 4.—OTHER END OF BRANCH SHOWN IN FIG. 3; THIS END HAS ESCAPED CHARRING.

entirely conclusive for it is now possible to view the intimate organizations of coals of every rank, grade, and description with the highest powers of the microscope. This possibility has not existed in the past and, as a consequence, works dealing with coal lack adequate illustrations of its structure. That situation is likely soon to be remedied. I have supplied a large number of illustrations for recent textbooks dealing with

geology, more particularly with the subject of coal. It would be out of place to describe the technical detail of these methods here, particu-

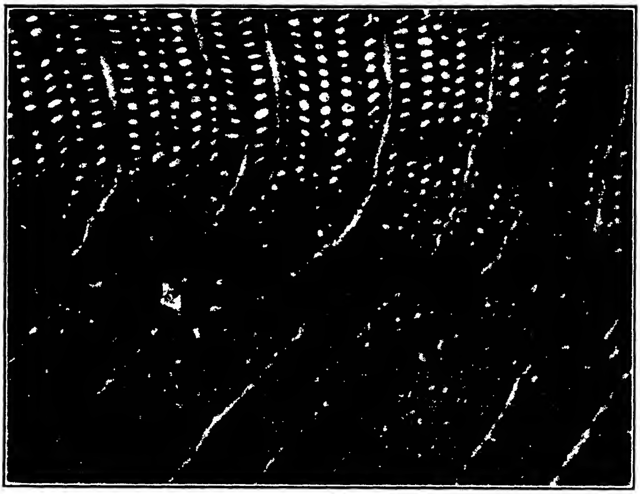

FIG. 5.—FRAGMENT OF WOOD FROM COAL SHOWING EFFECT OF CHARRING IN PRESERVATION OF WOOD STRUCTURE; UPPER PART IS CHARRED AND LOWER HAS NOT UNDERGONE THAT PROCESS.

FIG. 6.—VERTICAL SECTION OF A COAL BALL FROM LANCASHIRE, ENGLAND, SHOWING ORGANIZATION OF A PETRIFIED CONCRETION IN COAL.

larly as they have been stated in a memoir now being published by the American Academy of Arts and Sciences.

At present charcoal is still employed for smelting certain sorts of iron but, from the limited supply, its use is very restricted. It is proposed, in this paper, to show that coke bears an interesting relation, in origin, to the charcoal it has so completely replaced. The investigations of recent years have shown that coals consist, outside of their ash content, of three main materials more or less modified by water action, heat, and pressure. These constituents are present in different proportions in different coals and their relative abundance determines the general character of the coal. In certain coals, known as oil shales and cannels, the reproductive parts, or spores, of fernlike seed plants are present in large numbers. In many oil shales, spores greatly predominate over every other constituent; in cannels frequently they are much less abundant. Such coals yield large quantities of hydrocarbons, both gaseous and liquid, when subjected to dry distillation, either naturally or artificially. Coals of this type are usually characterized by a curved fracture and dull appearance, in contrast to the prismatic fracture and glistening aspect of coals of the bituminous and anthracitic types. The spore coals are an important source of petroleum and, consequently, occupy an outstanding position in the activities of the present age as the internal-combustion engine is actuated by their products. Coals of this type, in addition to the spores which are nearly always well preserved, even if much flattened by pressure, have a dark matrix which is penetrated by light only in sections 0.0001 in. thick or even thinner. As this material is entirely structureless, it is impossible to make more than a plausible surmise as to its nature. Judging, however, from the organization of accumulations of the present age, which resemble in general structure oil shales and cannels, it is highly probable that this dark matrix, which is so commonly present in spore coals, represents the more perishable parts of plants such as gelatinous cell walls, etc.

The third constituent of coals is wood. This is often extremely abundant and may exclude, in some cases, the spores and dark matrix that predominate in the spore coals, known as oil shales and cannels. The coals of this type, instead of having a conchoidal or curved fracture and a dull aspect, break up into prismatic fragments and are conspicuous for their glistening appearance. These glance or glistening coals supply us with the types known as bituminous coals and anthracites. In these the three constituents described are of different colors. The spores are golden yellow, the matrix when present is black, and the woody constituents have a rich brown hue. The general aspect of a thin section of coal, consequently, presents a striking and even gorgeous combination of colors, when examined by transmitted light under the microscope.

The general subject of the organization of coal has been dealt with by Doctor White and Doctor Thiessen, and the structure of anthracite by Professor Turner. It is possible, accordingly, to confine this paper to the

Fig. 7.—Vertical section of coal surrounding the coal ball; the raw materials of this coal consisted of woody fragments of plants and have entirely lost their structure except where they have been petrified, as in Fig. 6.

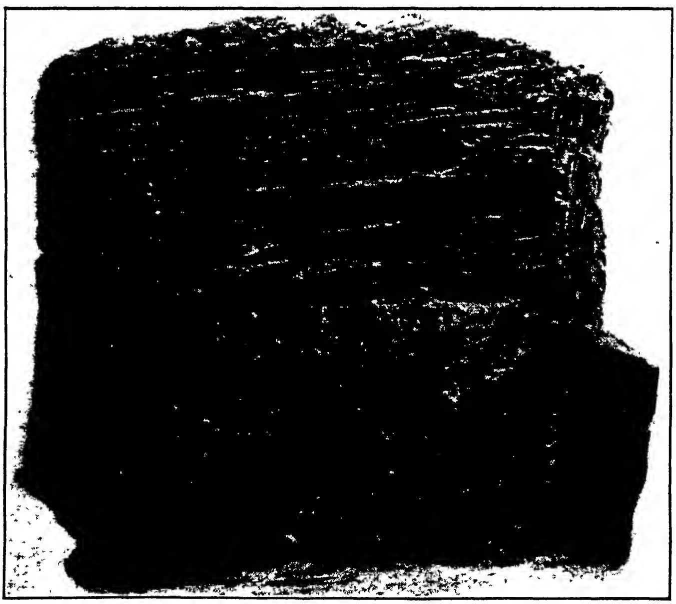

Fig. 8.—Gross aspect of a fragment of coal showing transition from bituminous coal to cannel; the bituminous is uppermost and the cannel coal below.

composition of coking coals in relation to their organization and origin. Fig. 12 shows the organization of coking coal of high rank from Connellsville, Pa. The coal, as a whole, is made up of a more or less homogeneous, but somewhat fissured, matrix that in nature is brown in color. The dark band running across the center represents partly charred wood, or fusaine often inaccurately described as "mother of coal" or "mineral charcoal." An examination of a wide range of coals shows that a great part of the brown matrix, which constitutes the mass of glistening coals with prismatic fracture, namely, bituminous coals and anthracites, is of woody origin; it is possible to trace in certain coals every gradation from wood with its structure perfectly preserved to that in which all trace of structural organization has disappeared. This possibility is presented in the case of fragments of wood or whole trunks or branches that have been partly charred by fire previous to inclusion in the raw material of the coal. The degree of charring marks the extent to which the original structure will be maintained in the fully matured coal, while complete absence of the action of heat creates a situation that often leads to the entire obliteration of structure in the course of ages. Between these two extremes lie imperceptible gradation, depending on the degree of exposure to heat. Illustrations of these modifications are shown in Figs. 3 to 5.

It follows from the statements regarding the woody origin of brown-hued materials in thin sections of coal, that the coking coal from the Connellsville basin referred to consists mainly of woody materials, or rather of materials of woody origin. The valuable coking and steam coal, commercially known as Pocahontas coal, shows an organization very similar to that presented by Connellsville coal. It follows naturally that if the theoretical views just expressed concerning the origin of Connellsville coking coal are correct, they apply equally to Pocahontas coal.

Without exception, typical oil-shale and cannel coals are entirely refractory in the coking oven and do not give utilizable coke. In the case of oil shales, this condition is apparently absolute; in the case of cannel coals, which often exhibit considerable brown matrix in addition to the yellow spores, at best a light almost flocculent coke is produced. This is of slight value for household purposes and is not to be considered at all for utilization in the blast furnace.

Impressed by the organization of such highly valued coking coals as those from the Connellsville and Pocahontas areas, it has seemed to the author that the worth of the coal, from the standpoint of the coking industry, was in direct proportion, other things being equal, to its content of modified wood (Lignitoid, Jeffrey; Anthraxylon, Thiessen). An attempt was made to verify this hypothesis experimentally. Cretaceous lignites representing the trunks of trees, the affinities of which have been accurately

determined by the microscope, were subjected to strong heat in a closed crucible. In a number of instances these woody trunks, which have been much modified during long ages by the action of water, pressure, etc.,

Fig. 9.—Vertical section through bituminous part of coal shown in Fig. 8; this coal consists mainly of structureless wood and of spores.

Fig. 10.—Vertical section of bituminous coal from Lancashire, England, showing large quantities of spores as well as modified wood.

gave rise to quite typical coke. Fig. 11 shows the formation of the coke resulting from the heating of one of these woods in a confined space.

Obviously, the organization has largely disappeared as the result of the liquefaction following exposure to high temperature. The author has carried on a number of experiments of this kind in the case of fossil woods

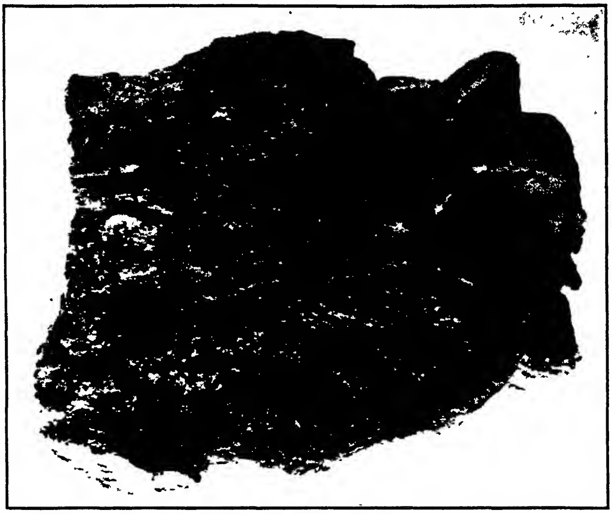

FIG. 11.—GROSS APPEARANCE OF CRETACEOUS TREE TRUNK THAT HAS BEEN TRANSFORMED INTO COKE BY HEATING IN A CLOSED CRUCIBLE.

FIG. 12.—VERTICAL SECTION OF COKING COAL FROM CONNELLSVILLE AREA; THIS IS MOSTLY COMPOSED OF MODIFIED WOOD, NEAR THE CENTER IS A SMALL FRAGMENT OF CHARRED WOOD IN TRANSVERSE SECTION.

from different geological periods. In many cases, the result has been the formation of a quite typical coke, while in other instances no coke resulted. In the latter cases, a process of charring was obvious but there

was no liquefaction followed by the formation of coke. As the structural organization of all the materials used in the present connection was purely woody, it follows that, in some instances, the wood had not undergone the chemical changes necessary to yield coke after being heated. It seems clear from the experiments described here and the illustrations that woody organization is a fundamental feature of the coals that can be transformed into coke in the oven; it follows, therefore, that not only must wood be the predominant constituent of the original raw materials of the coking coals, but it must have attained an appropriate degree of chemical modification. It is entirely likely that where time and nature have not brought the woody raw materials of the coals into a condition fit for coking, the knowledge and ingenuity of man can take the place of the slow processes of nature. It seems entirely probable, accordingly, that in the process of time, and as a result of our increase of knowledge of the chemistry of coal, all combustible minerals of mainly woody origin can ultimately be transformed into utilizable coke.

The author has one interesting example of a natural coke derived from a recent coniferous wood, which affords confirmation of his hypothesis that coking coals are formed of what was originally woody material. The specimen, dug up under a shallow covering of sand on Cape Cod, was sent to Prof. J. B. Woodworth with an inquiry as to its nature. He submitted it to the author, who discovered it to be a fragment of recent lignite, in a fair state of preservation, that had been partly transformed into coke.

If the views set down here are correct, coke has the same botanical origin as the charcoal it long ago replaced in the metallurgical industries. It follows, of course, that the original wood must have undergone the requisite chemical modifications in order to produce the substance known as coke. It is further clear that the presence of spore material, in any considerable amount in coking coals, is disadvantageous and that a large amount of spores effectually nullify the value of the coke that can be produced from any coal. A similar statement holds for those problematic organisms, which have been interpreted by some of my colleagues, as the remains of algae. They not only present all the optical characteristics of spores but are likewise disadvantageous as a constituent of coal for coking purposes. Pure spore coals, whether they be regarded as such or considered to be of algal origin, are quite incapable of undergoing the process of liquefaction under high temperatures to which the name coking is given.

DISCUSSION

David White,* Washington, D. C.—A few of the slides look as though they had been treated by chemicals, either acids or oxides, before or after grinding. What is the maximum temperature developed in these

* Senior Geologist, U. S. Geological Survey.

slides in the course of their preparation? Most of the sections shown represent genuinely aquatic deposits laid down in ponds and lakes rather than normal coals. Some of the slides first exhibited are essentially what was described by Potonié as sapropel. In the small lake or pond, which may be 50 feet deep and which in any event is too deep for the growth of subaerial vegetation in place, the deposit will contain much sapropelic material. The shorter the radius of the water-body, the nearer the shore to all parts of the area of accumulation, and the greater the opportunity for infall or drift of carbohydrate land vegetation into the aqueous deposit. Therefore, small sapropelic deposits like the typical cannel coals, which are laid down in ponds or little lakes, or in the sluggish cut-off bayous in the swamp, may contain considerable drifted wood or other detritus, as well as windblown spores, drifted pollen, and other small resistant debris.

The greater the extent of the water-body the less the amount of contributed debris of land origin and the greater the proportion of distinctly aquatic life. The canneloid type, which is shown in about half of Doctor Jeffrey's slides, is distinctly an aquatic deposit of the former (small lake or bayou) type and is not typical of our coals, which are generally xyloid. One does not think of a forest bordering the bayou or lake without shedding its pollen or dropping its leaves and twigs where they may blow or drift into the pond. The spores shed from the ferns are transported for long distances in the air and, together with the pollen grains, are characteristic if not dominant in the open-water deposits of the canneloid type. Again, the larger this body, the smaller in general will be the proportions of land derived spores or of pollen.

If the conditions of deposition are such as to permit oxidation and so to interfere with the concentration of ulmic matter to the point of toxicity to the germs, the woody material will continue to decay, for the most part, at least, as is usually found to have been the case in the canneloid deposits. Even in the terrestrial swamps aeration or slowness of accumulation of plant detritus may permit the loss of nearly all the woody material, leaving only the most resistant plant elements, such as spore and pollen exines, resins, and fragments of cuticles to survive in the deposit. Accordingly, we have, in passing from layer to layer in most coal beds, great variation in the amount of spore and other ultra-resistant debris, while in other layers greater toxicity of the aqueous medium has caused the conservation of more of the wood and other less resistant plant structures. In most deposits great amounts of plant matter are sacrificed before effective toxicity is reached through the accumulation of the ulmic products of smothered decomposition.

Cannels intergrade through the larger lake deposits into oil shales and bituminous shales in general.

Striped or "banded" coals are quite normal, in fact they are most common. The amount of wood in the ordinary coal may be from 15 to 85 per cent. or more, according to the condition of deposition. If the preservation of the wood is good, the wood is much more in obvious.

I am a little uncertain as to whether the author concludes that all the mineral charcoal scattered here and there in his peat deposits or pond deposits, become charcoal after burial of the deposits, or whether it came into the deposit as charcoal.

E. S. SINKINSON, Bethlehem, Pa.—What is it in coal that goes to form coke? Can it be the gases produced by a thermal decomposition of coal decomposing to give a nucleus of carbon in so fine a state of division that forces of cohesion come into play which bind them into the foundational structure of a coke?

S. W. PARR,* Urbana, Ill.—Are these zones where charring has taken place burning in the ordinary sense, or after being closed and subjected to geological conditions?

JAMES F. KEMP,† New York, N. Y.—Several times, in the past twenty-five years, when there have been severe forest fires in the Adirondacks charred leaves have come floating down out of the atmosphere and gently deposited on the surface of Lake George. All the discussion has assumed that the charred material would be deposited in a coal seam through the urgency of water, but the rush of hot air in a forest fire carries charred leaves up into the air and they are transported miles before they come down. Many times the fires were so far away we had no information as to the location; they were perhaps 25 miles away from the lake.

I could not help but be impressed with the discussion that the increased combinations of coals, as against the vegetable materials, is largely a matter of oxidization, whatever process we describe, whether the fraction or influence of bacteria make progressive anastomozing from vegetable matter to peat, so on to bituminous and anthracite, but with a progressive relative increase in the carbon. Just where we would draw the line in these processes between the oxidization and combustion, might be a difficult matter.

DAVID WHITE.—We are quite generally in agreement that ordinary coking coal represents the woody type of coal, whether lignite, subbituminous or semi-bituminous, which has been brought to the coking stage in the course of its evolution,—called carbonization or devolatilization. The coking qualities are generally excellent when the fixed carbon (pure coal basis) of these woody coals approximates 65 to 75 or is even as

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* Professor of Applied Chemistry, University of Illinois.

† Professor of Geology, Columbia University.

high as 83 per cent. "Mineral-charcoal" (fusain) is generally abundant in coking coals.

Edward C. Jeffrey.—As regards the nature of coking, I may say that wood of the same geological age, undoubtedly pure wood (I mean pure as regards structure) that has undergone the lignitic modification, can be coked in an ordinary closed retort; others cannot. That is the result of a degree of chemical modification that the original wood has undergone. I understand that it has been found possible to transform the ordinary wood into a substance like coal by heating it in vacuum for a prolonged period.

The microscopic study of this coke—and I have been able to get every stage of the modification from the original lignitic material to coke—shows that it is not any resinous material which is responsible for the coking unless that resinous material is secondarily derived from modification of the walls of the elements of the wood. In the preparations, you can see the walls melt and run together with the development of a moderate amount of gas, which is responsible for the porousness of coke. The piece of natural coke from Cape Cod was dug up under several feet of sand; it was not in the water at all. It may have been in the water at some time, but not in recent times at any rate.

I said at the outset that I was not dealing with chemical matters at all; all I claim is the structure of the coal is not modified. I have studied ground sections and sections of coal side by side, and where there is no difference between structure. I have found in sections very minute and delicate structures, and I am afraid the work will outlast my power. In the case of Mesozoic substances, the charred material can get in the water and come to rest without injury, even when it is of very delicate origin.

Reinhardt Thiessen,* Pittsburgh, Pa.—I have found invariably with ordinary bituminous coals, even those coals called non-coking, that that part of the coal derived from the woody parts of plants, which I call anthraxylon, cokes; the attritus in the same coal does not coke. In the typical coking coals, the resinous and the spore matters have largely disappeared and the woody derivatives have remained. For example, in tracing the Pittsburgh from its extreme western limits to the east, the coking properties of that coal increase. As the region of the typical coking coals is approached, the spore-matter disappears until, as at Connellsville, it has disappeared altogether. Why those spores should have disappeared I do not know. That the coal once did contain spores is shown by the cavities in which they were once located. The resinous matters have been charred or devolatilized so that they are opaque. It seems then that the woody parts of the plants have furnished

* Research Chemist, Bureau of Mines.

the coking constituents of coal. But in order to be coking, favorable factors must coincide.

Chas. R. Fettke,* Pittsburgh, Pa. (written discussion).—Several years ago, while engaged in an investigation of the oil resources in coals and carbonaceous shales of Pennsylvania for the Pennsylvania Geological Survey, the writer made a series of low-temperature carbonization tests on samples from all the known cannel coal deposits in the state. Since that time tests have also been made on oil shales from numerous other localities, including samples from different beds in the Green River formation of Colorado and Utah. While in most instances, the cannel coals and oil shales show little or no tendency to coke, there are some notable exceptions.

Among samples of cannel coal and shale representing thirty-one localities in Pennsylvania, three were found that possess the coking property to a rather marked degree. As a rule, cannel coals have a higher ash content than ordinary coals; this is particularly true of the Pennsylvania occurrences. The deposits that have been mined on a small scale in the state in recent years contain from 11 to 27 per cent. of ash; only four samples were obtained that contained less than 20 per cent. It seems likely, therefore, that in some instances at least the high ash content has affected the coking properties.

The purer portions of the famous Cannelton bed of cannel coal in the northwestern corner of Beaver County, Pa., form a hard dense coke. Pores, while numerous, are not as large as those ordinarily developed in coke from bituminous coking coals. Occasional fragments of unfused material, undoubtedly representing bony streaks in the cannel coal, are embedded in it. These are no more numerous, however, than in the cokes derived from many ordinary bituminous coals. The cannel coal on heating fuses and, at first, swells somewhat but later shrinks in volume so that the resulting coke does not occupy the entire space of the original charge.

Fig. 13 shows the coke obtained in testing a sample, taken from near the center of the channel-like deposit, in a Bureau of Mines oil-shale assay retort. The coal was crushed to pass a 4-mesh screen. It yielded at the rate of 49 gal. of oil per ton and had the following composition: Moisture, 1.26 per cent.; volatile matter, 44.49 per cent.; fixed carbon, 34.28 per cent.; ash, 19.97 per cent. A sample from near the edge of the deposit, which contained 27.48 per cent. ash, showed only a slight tendency to coke. Inasmuch as the spent material from this sample contained 44.2 per cent. ash, the difference in behavior can be readily accounted for.

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* Associate Professor of Geology and Mineralogy, Carnegie Institute of Technology.

Doctor Thiessen has made microscopic studies of the samples tested and has found that the Cannelton deposit, which occurs at the Upper Kittanning horizon, represents a typical spore cannel coal. Photomicrographs of this coal are shown in previous publications by the writer.[1]

Another cannel coal that forms a hard dense coke was obtained from what is also probably the Upper Kittanning horizon in the country bank of G. W. Currie, 2 miles north of Nealeys, Butler County, Pa. It yields

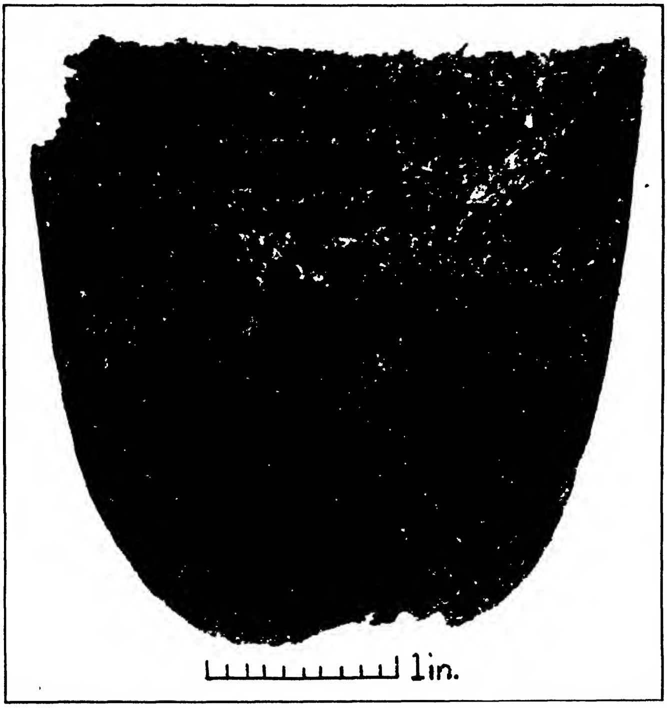

FIG. 13.—COKE FROM CANNELTON, PA., CANNEL COAL.

at the rate of 33 gal. of oil per ton and has the following composition: Moisture, 0.83 per cent., volatile matter, 38.94 per cent.; fixed carbon, 49.14 per cent.; ash, 11.09 per cent. Doctor Thiessen classifies it as a humic type of cannel coal. Photomicrographs are shown in the publications just referred to (Pl. IV, Fig. A; and Fig. 2, page 1169, respectively).

The third sample of cannel coal that forms a hard porous coke came from a deposit at the Upper Kittanning horizon near the head of Crooked Run, 3 miles south of Savan in Indiana County, Pa. It yields at the rate

[1] Oil Resources in Coals and Carbonaceous Shales of Pennsylvania. Pennsylvania Geol. Surv. (1923) Pl. II, Fig. C; Cannel Coal and Carbonaceous Shale Deposits of Pennsylvania. *Trans.* (1923) **69**, 1169, Fig. 1.

of 19 gal. of oil per ton and has the following composition: Moisture, 0.53 per cent.; volatile matter, 27.64 per cent.; fixed carbon, 53.98 per cent.; ash, 17.85 per cent. The low percentage of volatile matter is undoubtedly due, in large part, to the fact that the deposit occurs in an area in which the coals have been subjected to a greater degree of metamorphism. While the bituminous coals of Beaver and Butler counties contain from 55 to 63 per cent. of fixed carbon, computed on a pure coal basis, those of Indiana County contain from 63 to 79 per cent. Unfortunately, no microscopic studies have been made of specimens from this locality.

Dunlap,[2] in carrying out carbonization tests on Missouri cannel coals has also found a wide range in their coking properties; out of four samples tested, only two gave coke of commercial value. According to this investigator, the Bunceton cannel coal from Cooper County, Mo., yields a very good coke. It is hard and the entire charge fuses together; the porosity is about the same as that of ordinary coke. The Stover cannel coal, from Morgan County, Mo., also yields a good coke, but it is high in sulfur. The Bunceton coal contains 8.16 per cent. ash and yields at the rate of 53.5 gal. of oil per ton; while the Stover coal contains only 2.3 per cent. of ash and yields at the rate of 64.88 gal. of oil per ton. Microscopic studies of these coals to determine the type of cannel coal represented would be desirable.

Some of the richer oil shales from the Green River formation of Colorado, examined by the writer, show a decided tendency to fuse when heated. The crushed shale, when carbonized in a closed retort, fuses completely and shrinks markedly in volume. The resultant mass clings tenaciously to the walls of the retort and is difficult to remove. This property will have to be taken into consideration in designing retorts to treat this particular type of shale. Other oil shales in the same formation, equally rich as far as yield of oil is concerned, show practically no tendency to fuse. Finley, Horne, Gould, and Bauer[3] have also called attention to this tendency of certain oil shales to coke. Of course, the term coking as applied to oil shales does not mean that a metallurgical coke is produced. There is, however, a certain resemblance in behavior between these oil shales and ordinary bituminous coking coals when they are undergoing carbonization.

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[2] Howard Leroy Dunlap: The Carbonization of Missouri Cannel Coals. *Bull.* Missouri School of Mines (1919) **5**, No. 1, 49.

[3] W. L. Finley, J. W. Horne, D. W. Gould, and A. D. Bauer: Assay Retort Studies of Ten Typical Oil-Shales. Reports of Investigations, Bureau of Mines, Ser. No. 2603 (1924) 6.

Resolution of Coal by Oxidation

By W. Francis* and R. V. Wheeler,† Sheffield, Englind

(New York Meeting, February, 1925)

Of the methods that have been used for studying the chemical composition of coal, attack by reagents has not, in general, yielded much information. Most of the reagents used have been strong oxidants such as nitric acid or Schulze's solution. The use of a milder oxidizing agent, such as air at low temperatures, enables progressive changes in the character of the coal substance to be studied and thus helps toward an understanding of its constitution.

British bituminous coals frequently have a banded structure. These bands (of four types) can be separated one from another and have been found to possess markedly different chemical characteristics, even when taken from contiguous portions of the same lump coal. It has been found convenient to give each of the ingredients of banded coal a distinctive name, more or less descriptive of its appearance, and the study of the chemistry of bituminous "coal" in England has resolved itself into a study of each ingredient separately.

The coal chosen for this work was taken from the Top Hard seam at East Kirkby colliery, Nottinghamshire, a detailed chemical analysis of which has been recorded by Baranov and Francis.[1] The banded structure was well marked and the bands could readily be separated. The research was confined to the brilliant vitreous bands (*vitrain*), the dull hard bands (*durain*) and the "sooty partings" (*fusain*); for previous work had shown that the fourth type, to which the name *clarain* has been given, is intermediate in character, chemically, between vitrain and durain.

The method of experiment was, briefly, to draw a slow current of moist air through weighed samples (50 gm.) of the three ingredients, vitrain, durain, and fusain, in the form of powder (through a 60-mesh and on a 90-mesh sieve) contained in glass tubes which could be maintained at a constant temperature during prolonged periods. After passing through the coal, the air bubbled into a measured volume of

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[1] *Fuel in Sci. & prac.* (1922) 1, 219.

cold distilled water to condense or dissolve any gaseous products of the oxidation. At stated intervals (usually 1 month) for each temperature employed, this water was examined and changed and a small fraction (5 gm.) of each coal was removed from the tubes for analysis. The temperatures used in the oxidation were 100° C., 150° C., and 200° C., and the total time allowed for oxidation at each temperature was 5 months, 6 months, and 6 weeks respectively.

Liquid and Gaseous Products

The chief products identified were formaldehyde, methyl alcohol, and the lower fatty acids. During oxidation at 100° C., these were obtained in small quantities from all three ingredients; but at higher temperatures, the vitrain and durain produced only traces of formaldehyde and acids and the fusain none at all.

Changes in Composition

Table 1 shows the progressive changes in weight as the oxidation proceeded. A loss in weight, which was most marked during the oxidations at 200° C., caused a corresponding increase in ash content.

Table 1.—*Changes in Weight as Result of Oxidation*

	Change in Weight			Ash Content		
	Fusain, Per Cent.	Durain, Per Cent.	Vitrain, Per Cent.	Fusain, Per Cent.	Durain, Per Cent.	Vitrain, Per Cent.
Original	....	....	....	17.78	4.05	1.14
100° C. I	+ 0.66	+ 0.7	+ 1.74	17.57	4.06	1.37
II	− 1.0	− 1.5	− 0.2	17.77	3.95	1.56
III	− 1.0	− 0.58	− 0.7	17.80	3.80	1.78
IV	− 0.1	+ 0.1	nil	17.96	3.95	1.76
150° C. I	− 3.26	− 4.59	− 8.79	17.98	4.73	2.22
II	− 4.4	− 5.55	− 7.3	17.90	4.86	2.15
III	− 0.86	− 3.0	− 0.22	18.25	4.95	2.17
200° C. I	−19.7	−23.5	−27.0	21.4	6.45	2.85
II	− 7.0	− 7.4	− 7.2	21.51	6.5	2.8

Proximate Analysis

The volatile matter (see Table 2) calculated on an ash-free, dry basis, showed but small fluctuations during oxidation at 100° C., the net result being a slight gain with the fusain, a slight loss with the durain, and little change with the vitrain. On oxidation at 150° C., however, all showed a greatly increased content of volatile matter. This was greatest with the vitrain and the change was completed during the first period of

heating (2 months). With the durain and the fusain, the volatile matter increased more gradually and the change may not have been completed during the 6 months the experiment lasted. On oxidation at 200° C., the volatile matter of the vitrain showed a decrease. This fact, together with other observations discussed later, suggests that decomposition of the oxidized product had begun. Both the durain and fusain showed a slight increase in content of volatile matter.

TABLE 2.—*Proximate Analysis, Percentages on Ash-free Dry Coal*

	Volatile Matter, Ash-free Dry Coal			Ulmins		
	Fusain, Per Cent.	Durain, Per Cent.	Vitrain, Per Cent.	Fusain, Per Cent	Durain, Per Cent.	Vitrain, Per Cent.
Original	19.84	28.91	30.74	nil	0 01	0 02
100° C. I	23 69	26.55	31.01	1 2	2.6	11.17
II	22.22	25.60	30 69	1 8	5.58	11.25
III	20 98	27.08	31.16	1 7	6.60	11.30
IV	20.78	27.04	31.06	2 2	6 52	11.20
150° C. I	25 9	31.8	40 75	14 25	36.1	93.5
II	25.9	32.1	40 4	19.5	43 5	97.0
III	27.1	32.2	40 5	24 0	46 0	95.5
200° C. I	29.8	37.8	38 5	20 5	64.0	70.0
II	31 2	37.1	39 0	22 0	65 0	75.0

These results can be explained by the determinations of the amount of ulmins (compounds soluble in caustic alkalies) present. After oxidation at 150° C., the coals contained large quantities of ulmins and their properties then became largely those of the ulmins they contained. The volatile matter of the ulmins is high (about 41 per cent.) and the volatile matter of the coals oxidized at 150° C. approached this figure as their ulmin contents approached 100 per cent.; while during oxidation at 200° C. there is evidence of decomposition. The coking properties of the vitrain were completely destroyed after 2 months oxidation at 100° C. Neither the durain nor the fusain formed a coherent coke either before or after oxidation.

Table 3 shows the effect of oxidation on the behavior of solvents toward the coal. The nomenclature proposed by Stopes and Wheeler has been used, in which the terms alpha, beta and gamma compounds are used, respectively, for the portions of coal insoluble in pyridine, soluble in pyridine but insoluble in chloroform, and soluble in both pyridine and chloroform. It should be noted, however, that the character of these fractions is not necessarily the same for both the unoxidized and the oxidized coals.

TABLE 3.—*Solubility in Pyridine and Chloroform*

	Fusain			Durain			Vitrain		
	Alpha, Per Cent.	Beta, Per Cent.	Gamma, Per Cent.	Alpha, Per Cent.	Beta, Per Cent.	Gamma, Per Cent.	Alpha, Per Cent.	Beta, Per Cent.	Gamma, Per Cent.
Original	95.2	3.4	1.4	90.5	6.8	2.7	79.7	14.6	5.7
100° C. I......	95.2	3.35	1.45	90.0	7.05	2.95	85.6	10.4	4.0
II.	96.54	?	?	90.0	?	?	85.4	11.0	3.6
III.	95.0	3.5	1.5	87.9	9.2	2.9	87.6	9.6	2.8
IV.. ...	94.15	4.45	1.40	87.6	9.4	3.0	87.6	9.9	2.5
150° C. I.	94.5	5.5	Trace	87.4	12.1	0.5	75.95	23.2	0.85
II .	82	18	Trace	80 3	19.7	Trace	57.7	42.3	Trace
III	80	20	nil	77.0	23	nil	55	45.0	nil
200° C. I .	89	11	nil	78.0	22	nil	72	28	nil
II . .	85	13	nil	76	24	nil	70	30	nil

As with the contents of volatile matter, the differences due to oxidation at 100° C. were small. A fact that the figures do not show is that the beta compounds of the oxidized coal were largely ulminified. There was a tendency for the gamma compounds of the vitrain to lose their solubility in chloroform on oxidation even at 100° C., while after oxidation at 150° C. this solvent extracted very little, if anything. Similarly, with the durain and the fusain, no gamma compounds were present after oxidation at 150° C.

With all the coals, there was a marked increase in solubility in pyridine, up to a maximum of 45 per cent. observed with the vitrain (coincident with the maximum formation of ulmins).

Ultimate Analysis

The vitrain, durain, and fusain from the original Top Hard coal showed the same gradations in ultimate analysis as were found by Tides-

TABLE 4.—*Ultimate Analyses, Percentages on Ash-free Dry Coal*

	Fusain			Durain			Vitrain		
	Carbon, Per Cent.	Hydrogen, Per Cent.	Oxygen, etc., Per Cent.	Carbon, Per Cent.	Hydrogen, Per Cent.	Oxygen, etc., Per Cent.	Carbon, Per Cent.	Hydrogen, Per Cent.	Oxygen, etc., Per Cent.
Original	85.95	3.86	10.19	81.75	4.83	13.42	79.71	5.17	15.12
100° C I...	83.13	3.51	13.36	77.62	3.89	18.59	74.3	4.16	21.64
II...	81.32	3.25	15.43	76.13	3.70	20.17	72.19	3.95	23.86
III...	81.08	3.30	15.62	76.08	3.67	20.25	71.90	3.79	24.31
IV...	81.08	3.29	15.63	76.47	3.71	19.82	72.08	3.86	24.06
150° C. I...	77.86	2.45	19.69	71.94	2.55	25.51	66.45	2.69	30.86
II .	73.9	2.31	23.79	68.9	2.61	28.49	64.73	2.50	32.77
200° C. I...	72.8	1.8	25.4	69.8	1.8	28.4	65.8	2.0	32.2
II...	71.3	1.6	27.1	70.0	1.76	28.24	65.6	2.01	32.39

well and Wheeler[2] for Hamstead coal. During oxidation of the Top Hard coal, there was a progressive loss of carbon and hydrogen and an increase of oxygen. The amount of oxygen reached a maximum with the vitrain at 150° C., when the coal substance had been completely converted into ulmins. When decomposition of the ulmins by heat began (at 200° C.), the oxygen content was slightly decreased owing to the elimination of carbon dioxide. Analyses of the durain and fusain gradually approached that of the vitrain but never quite reached it, because of the presence of some portions of the coal conglomerate that were difficult or impossible to oxidize.

The analyses of the ulmins produced from all portions of this seam of coal were similar. This fact, together with the similarity of the analyses of the gases produced on their destructive distillation (see later), indicates that the ulmins produced by oxidation of all parts of the same seam of coal have the same composition. The analyses of these ulmins averaged: Carbon, 64.5 per cent.; hydrogen, 2.8 per cent.; oxygen, etc., 32.7 per cent. and they contained 41.5 per cent. of volatile matter. They were completely soluble in ammonia and in solutions of potassium and sodium hydroxide, and potassium and sodium carbonate; while pyridine dissolved about 51 per cent. They were insoluble in chloroform.

TABLE 5.—*Percentages of Nitrogen and Sulfur*

	Fusain, Per Cent.	Durain, Per Cent.	Vitrain, Per Cent.
Nitrogen:			
Before oxidation	1.29	1.65	1.68
After oxidation	1.3	1.91	2 28
Sulfur:			
Before oxidation	0.53	0 64	1.3
After oxidation	0.66	0.42	1.06
Sulfate Sulfur:			
Before oxidation	nil	nil	nil
After oxidation	0.26	0.18	0.18

In the figures for the percentages of oxygen, the nitrogen and sulfur present in the coals are included. During the oxidations no nitrogen was lost, but the nitrogen-containing nucleus survived and appeared in the ulmins. The percentage of nitrogen in the oxidized coals was increased proportionally with their loss in weight. The sulfur in the original coal existed partly in inorganic form. During oxidation, a portion of this was evolved as sulfur dioxide and a portion changed from sulfide to sulfate. As a portion of the sulfur (organic) remained in the ulmins produced, it may be concluded that sulfur is also a con-

[2] *Trans.* Chem. Soc. (1919) **115**, 619.

stituent of this nucleus, though the quantity present is less than that of the nitrogen; see Table 5.

Oxidation by Hydrogen Peroxide

Ulmins may be produced from coal more quickly by chemical oxidizing agents than by atmospheric oxidation. The simplest and quickest oxidizing agent was found to be a solution of hydrogen peroxide. This has been used with a number of coals, usually in alkaline solution so as to obtain the ulmins in solution. Anthracites are not appreciably oxidized by hydrogen peroxide but lower grade coals soon become soluble in alkalies and the soluble portions continue to be oxidized until a limiting composition is reached agreeing closely with that of the ulmins formed on atmospheric oxidation. The upper limit of composition for ulmin compounds soluble in alkalies has been found to be about 70 per cent. carbon and 4.2 per cent. hydrogen and the lower limit about 62 per cent. carbon and 2.8 per cent. hydrogen. Below this limit of composition, the sodium salt of the ulmins could not be oxidized but the free acid was readily decomposed and during the decomposition the nitrogen contained in the compounds was evolved quantitatively as ammonia.

Destructive Distillation

An examination of the gaseous products of destructive distillation confirmed the resemblance between the ulmins produced from the vitrain and durain of the same coal. With both, decomposition began at as low a temperature as 150° C. and the gases evolved consisted entirely of oxides of carbon in the ratio $CO_2:CO$ of about 12:1. This ratio decreased as the temperature of decomposition was increased. No other gaseous products of importance were evolved below 450° C. when methane and hydrogen made their appearance. The chief results are recorded in Tables 6 and 7 and in Figs. 1 and 2.

A comparison of these results[3] with those for unoxidized vitrain on the one hand and dopplerite on the other reveals that the groupings in these two substances, from which unsaturated hydrocarbons (and some methane and hydrogen) are evolved, are absent in the ulmins from oxidized coal, which suggests that oxidation had caused a progressive splitting off of external groupings leaving a nucleus. This nucleus appears to be of the same character in dopplerite, vitrain, and the amorphous portions of durain, clarain, and fusain, and the first stage in the progressive oxidation of coal is a change from insoluble into soluble ulmins by a modification of the external groupings.

Oxidation of the nucleus, which contains both nitrogen and sulfur, is both rapid and complete when hydrogen peroxide is used, and the only

[3] *Trans.* Chem. Soc. (1922) **121**, 2345.

TABLE 6.—*Principal Gases Evolved on Destructive Distillation; Cubic Centimeters per Gram of Ash-free Dry Substance*

	Vitrain Ulmin								
Temperature, Degrees C.	160	210	260	310	360	410	460	520	580
Carbon dioxide	9.61	11.41	19.3	17 82	15.06	13.95	12.39	12.28	8.48
Carbon monoxide	0.74	0.99	0.98	0.91	1.14	1.34	1.60	3.23	3.89
Hydrogen	nil	nil	nil	nil	nil	nil	0.12	0.95	2.40
Methane	nil	nil	nil	nil	nil	nil	0.44	2.84	6.02
Ratio $\frac{CO_2}{CO}$	12.95	11 52	19 7	19.7	13.14	10.4	7.75	3.8	2.18

Analysis carbonized residue: Carbon, 80.6 per cent.; hydrogen, 3.4 per cent.; oxygen, etc., 16.0 per cent.

TABLE 7.—*Principal Gases Evolved on Destructive Distillation; Cubic Centimeters per Gram of Ash-free Dry Substance*

	Durain Ulmin								
Temperature, Degrees C.	170	220	270	310	370	410	470	520	580
Carbon dioxide	7.82	8.19	13.93	15 39	18 55	13.26	15.11	13.06	9.72
Carbon monoxide	0.58	0 62	0.80	0.87	1.52	1.35	2.15	2.76	3.71
Hydrogen	nil	nil	nil	nil	nil	nil	0.08	0.60	1.43
Methane	nil	nil	nil	nil	nil	nil	0.81	2.16	5.60
Ratio $\frac{CO_2}{CO}$	13.24	13.4	17 46	17.7	12.21	9.82	7.02	4.71	2 61

Analysis of carbonized residue: Carbon, 83.3 per cent.; hydrogen, 3.2 per cent.; oxygen, etc., 16.0 per cent.

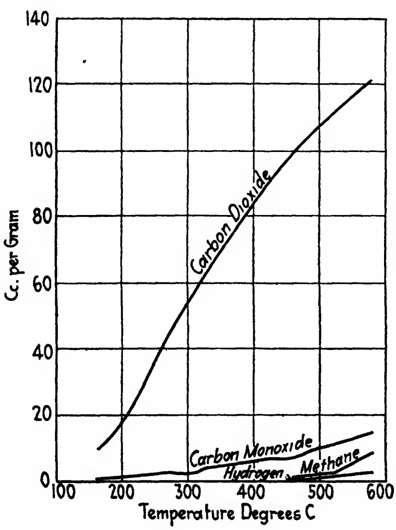

FIG. 1.—VITRAIN ULMINS.

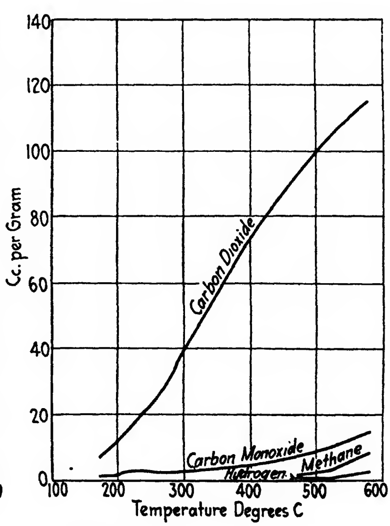

FIG. 2.—DURAIN ULMINS.

products so far isolated are monobasic and dibasic fatty acids, oxides of carbon, ammonia, and water. It is hoped, in future work, suitably to moderate oxidation of the nucleus so as to be able to isolate intermediate compounds.

Presence of Plant Debris

The treatment of coal with hydrogen peroxide has made possible a close study of those parts that do not become transformed into soluble ulmins. Microscopical examination has revealed that the residue consists of plant debris. In the residue from a fusain, wood tracheids have

Fig. 3.—Wood tracheid from fusain. × 140.

Fig. 4.—Parenchymatous tissue from durain. × 140.

always predominated (Fig. 3). The debris from the clarains and durains examined have differed but little from one another in general character. They are transparent and show a variety of recognizable structures, varying in color from deep red to pale amber, while some fragments are green as though the chlorophyl has been preserved. Spore exines and portions of epidermis are of frequent occurrence and fragments of soft-walled tissue are sometimes to be found. The surface views of the parenchymatous tissue isolated exhibit polygonal cell outlines, showing that the fragments are of epidermis of leaves or young stems. Many fragments of such tissues show the stomata in surface view (see Figs. 4, 5, 6, and 7) and are colored pale yellow and brown. Some thickened tissues are also present, of deep mahogany color, presumably the remains of the periderm. Microspore exines are numerous and their size and ornamentation varies considerably. The characteristic triradiate marking is often observable while a few of the spore exines have well developed

"wings" characteristic of the microspores of *Spencerites*. The megaspore exines are usually broken into small fragments, because of the grinding

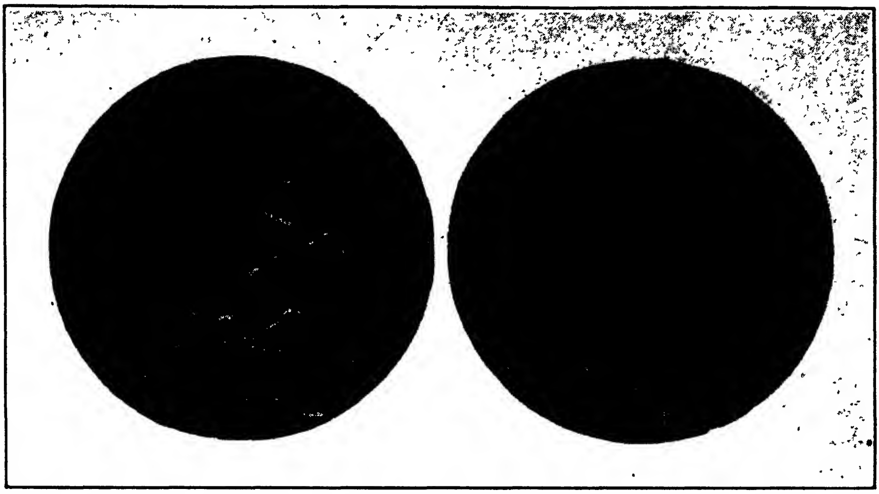

FIG. 5.—SAME SPECIMEN AS IN FIG. 4. × 280. FIG. 6.—PARENCHYMATOUS TISSUE FROM DURAIN. × 140.

the coals receive before their treatment with hydrogen peroxide but a few complete exines have been separated. These are almost spherical

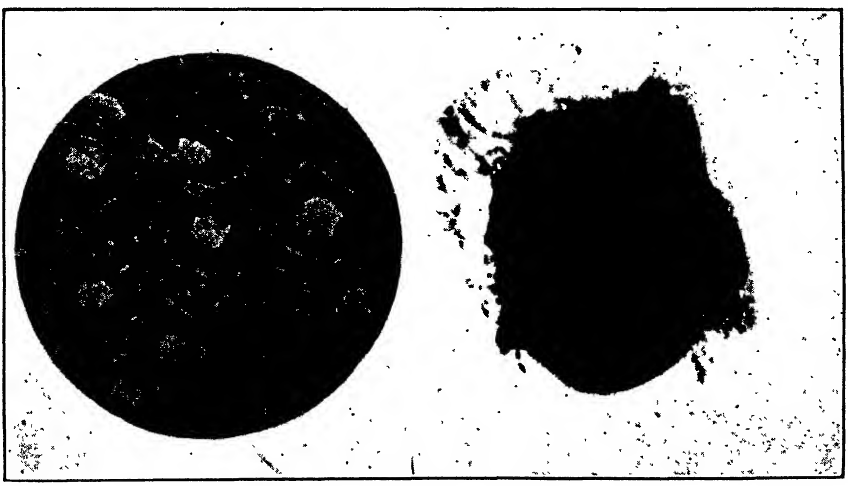

FIG. 7.—SAME SPECIMEN AS IN FIG. 6. × 280. FIG. 8.—SPORE EXINE FROM DURAIN. × 30.

bodies, dark brown in color, exhibiting triradiate marking and sometimes having hairs attached, as in some species of *Lepidostrobus* (Fig. 8).

In one coal examined (the Hamstead), the debris obtained after treatment with hydrogen peroxide contained minute amber-colored rods apparently containing no cell structure. Some of this debris was extracted with chloroform, which yielded a semi-solid brown mass having an analysis: carbon 80.3 per cent. and hydrogen 10.4 per cent. The rods thus appear to be resin and to be analogous to the resin rods observed by White in American coals.

Summary

The present work shows that alkali-soluble ulmins can be regenerated from a bituminous coal by mild oxidation. If the coal is a vitrain, it consists almost solely of ulmins; the transformation of insoluble to soluble ulmins in a clarain, a durain, or a fusain leaves residues characteristic of each of these ingredients, which are essentially the original plant entities that were particularly resistant to, or were preserved from, the process of "decay" that constituted the early stages of coal formation, and are, apparently, but little altered.

Bituminous coal, then, consists of insoluble ulmins in which are dispersed the morphologically organized plant tissues that have escaped ulmification.

DISCUSSION

Edward C. Jeffrey,* Cambridge, Mass.—Two or three years ago the president of the Chemical Society said that it was possible to treat almost any bituminous coal in such a way that it would coke; can anybody throw some light on that statement?

S. W. Parr,† Urbana, Ill.—On the border line, perhaps, are the Illinois coals, which are non-coking. I am quite sure they can be made to coke.

E. S. Sinkinson, Bethlehem, Pa.—Do the terms "durain," "clarain," and "vitrain" give any clearer understanding of the subdivisions of coal than do dull, bright, or glance? Are the captions of Figs. 4, 5, and 6 correct? They look like epidermis. In discussions on the composition of coal why are the nitrogenous contents so much neglected, when they are relatively so important?

Reinhardt Thiessen,‡ Pittsburgh, Pa.—Nitrogen in the coal is considered in my paper. Proteins are easily decomposed and their nitrogen is changed to ammonia, which escapes; but in the compounds I mentioned, the nitrogen forms part of a ring that is not broken up during decay.

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† Professor of Applied Chemistry, University of Illinois.

‡ Research Chemist, Bureau of Mines.

David White,* Washington, D. C.—A point in this paper that is specially interesting to me is the observation of the progressive increase in capacity for regeneration according to the amount of woody material in the coal, the reaction of the fusain ("mineral charcoal") being least, that of durain being intermediate, while in the bright stripes largely composed of ulmified wood it is very much greater. The ulmic matter, which forms the groundmass of the coal and is present in all coals, and is largely derived from carbohydrate or lignocellulosic material, is relatively more abundant in durain than in fusain, and is perhaps most abundant—at least in effect—in the so-called vitrain. In the woody material—assuming vitrain is woody, though it is so glassy, so completely impregnated, so homogeneously ulmified, as to be reluctant to reveal its woody structure—we have not only the carbohydrate derivative of the binder, but the carbohydrate derivative or transformed carbohydrates of the undecomposed woods. The latter have, of course, long since been chemically transformed beyond the celluloses or other carbohydrates as we now recognize them. It would appear either that the ulmic matter which so copiously impregnates and envelopes the woody tissue is more easily oxidized, or that the transformed carbohydrates of the wood itself so approach in chemical composition the ulmic matter as to play a similar role in the oxidizing process. On the whole, may we not infer that the capacity of these coals to oxidize, with the regeneration of ulmic matter, varies with the amount of ulmified wood as well as of ulmic binder in the coals of a given rank?

Edward S. Jeffrey.—Some years ago, a memoir on lignites was published from my laboratory, where the nuclei were shown. The situation would compare somewhat with Doctor Thiessen's remark in regard to the Connellsville coal; the spores were there.

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The Constitution of Coal

By F. V. Tideswell* and R. V. Wheeler† Sheffield, England

(New York Meeting, February, 1925)

Coal being essentially a complex conglomerate of plant remains that have undergone decay and interaction in varying degree, it is understandable that attack on the problem of its chemical constitution by normal chemical methods should have been attended by but slight success. The obvious method of fractionation by means of selective solvents has yielded a few results of some value. Thus it is known that from many, if not all, bituminous coals organic solvents extract small percentages of oxygenated compounds, which are generally assumed to have been derived from the original plant resins, though a more probable source would appear to be the glycerides and waxes of the plants. Organic solvents also extract small proportions of hydrocarbons, the origin of which is doubtful. Of more importance is the action of such pseudo solvents as pyridine, which, in addition to their specific solvent action, have the power of resolving and simplifying a portion of the coal substance in a manner analogous to that by which water can disperse a hydrogel. Early work with pyridine indicated that coals are composed of two main classes of compounds: the one soluble in organic solvents, the other capable of being partly dispersed in pyridine. Recent work has shown that the dispersion is colloidal in character and that it may be accomplished by the use of solvents less active than pyridine, such as benzene or chloroform, provided that the temperature of extraction is raised or the coal has been suitably preheated.

The action of reagents on coal has proved of little value in the past, but some insight into the constitution of coal has been given by regulated destructive distillation. Thus, it has been shown that coals behave on distillation as though composed of two main classes of compounds: the one readily decomposable at moderate temperatures (yielding mainly the paraffins), the other undergoing a preliminary early decomposition (with evolution of oxides of carbon and water) and yielding a residue that at higher temperatures breaks down, yielding much hydrogen.

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In view of the diversity of materials that enter into the composition of the coal conglomerate, success in determining the constitution of coal cannot be expected unless the character of each type of material is considered alone and until the extent of the contribution of each to the coal substance is known. A comprehensive scheme of coal research should, therefore, comprise a study of each individual plant entity or degradation product thereof that occurs in coal. This, broadly, is the basis on which investigations into the constitution of coal are proceeding in England under the Safety in Mines Research Board and in the Department of Fuel Technology of Sheffield University. Different programs of research deal with the contributions to coal of cellular tissue, of unorganized or amorphous material, such as the ulmins and the resins, and of structured materials such as cuticles and spore exines. Usually a preliminary inquiry into the chemistry of corresponding modern substances has proved necessary. For example, an investigation into the character of a peat ulmin (dopplerite) has shown a marked relationship between this and an amorphous portion of banded bituminous coal. Work designed to extend our knowledge of the constitution of the modern ulmins is now proceeding, together with an investigation of synthetic ulmins from various sources.

The natural ulmins, the brown amorphous products of plant decay, first attracted the attention of chemists on their extraction from the rotted wood of an elm tree[1] by alkaline solutions from which they were precipitated by acids as brown flocks. The solubility in alkalies and reprecipitation in an amorphous form on acidification were long used as the sole criteria of what constituted an "ulmin," but there is now considerable evidence that similar substances, insoluble in alkaline solutions, can with advantage be referred to under the same general name.

Ulmins are found in any substance derived from vegetable matter that has undergone moldering decay; for instance in soils, peats, and to a less extent in lignites and coals. The ultimate composition of all such ulmins is similar, ranging from 50 to 60 per cent. carbon, 4.5 to 6.0 per cent. hydrogen, 0.5 to 2.0 per cent. nitrogen, and 30 to 40 per cent. oxygen. Substances of similar type, but of somewhat different composition, have been obtained by the action of reagents on vegetable matter and by the treatment of such materials as sugars and derivatives of furan and phenol with boiling dilute acids. Other artificial ulmins are produced by the oxidation of lignin in the presence of alkalies, and by the condensation of sugars (and carbohydrates in general) with simple or complex amino acids. These reactions are of interest mainly because they suggest the manner of formation of natural ulmins.

[1] Thomson (1807) named them ulmins because of their original association with the elm (Latin *ulmus*).

The exact constitution of the ulmins is, at present, unknown. They appear to possess an acidic character, but the source of the acid function, whether phenolic or carboxylic, is undecided. The natural ulmins appear to be related, in structure, to the lignin and cellulose of the cellular tissues of the plants from which they were formed, for alcoholic hydroxyl groups are present in large proportions, while methoxyl groups are also found. Fischer and Schrader[2] consider the lignin alone to have provided ulmins when the plants decayed, while Marcusson[3] thinks the cellulose was chiefly responsible. From our own examination of peat ulmins, we are disinclined to argue, with either Fischer and Schrader or Marcusson, their formation from one class of original plant substances to the exclusion of another class, or to argue the survival in them of the lignin complex to the exclusion of the cellulose, or *vice versa*. We have observed some evidence of a carboxylic acid function in peat ulmins, while the hydroxyl content appears to be almost 30 per cent. of the whole. Destructive distillation discloses resemblances with both lignin and cellulose, while the nitrogen present appears to be very firmly linked. We conclude that the peat ulmins, considered to have been derived from degraded celluloses, lignocellulose and proteins (condensed together with partial dehydration as with the amino-ulmins of Maillard) still preserve the original lignin and cellulose groupings, together with new ringed structures containing oxygen and nitrogen. The formation of ulmins in nature appears to have been due to chemical rather than bacterial action, and of the various suggested chemical reactions that between carbohydrates and amino-compounds (probably following their liberation by bacterial action) seems the most likely.

The extent of the contribution of the ulmins to coal has occasioned much debate. Without reverting to the extreme conception of the "fundamental jelly" of Fremy, we consider as the result of recent work that many, if not most, British coals consist largely of ulmic material. This view is not inconsistent with the presence of the wealth of plant materials that are visible in transparent sections of most coals. Despite their number, the contribution of these by weight is not necessarily large.

It is of interest to trace the changes that we may suppose have taken place during the aging of a deposit of plant remains. The original material may be compared with peats of various ages (as representing a conveniently studied form of partly degraded plant débris) and with coals. The various plant entities and residues that have contributed to the formation of the organic substance of coal can conveniently be grouped according as they are:

1. *Resistant to decay:* Among the more important members of this group are: (*a*) Spore exines and cuticular tissues; and (*b*) resins.

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[2] *Brennstoff Chem.* (1921) **2**, 23.
[3] *Ztschr. f. angew. Chem.* (1923) **36**, 42.

2. *Subject to decay:* The members of this group are either: (*a*) Organized, such as cellulosic and lignified tissues; or (*b*) amorphous, the contents of plant cells.

3. *The products of decay:* The ulmins.

An accumulation of plant remains immediately after deposition consists mainly of the first two groups, but in an older deposit, such as a peat bed, certain changes have taken place. The members of group 1 are still present in an apparently unaltered form. The cellulose and lignin of the group 2, however, have suffered decay, undergoing such minor alterations as dehydration produces, or becoming ulmified (probably in conjunction with certain of the cell contents), or disappearing altogether. According to Fischer and Schrader,[4] the lignin alone survives in any form, the cellulose of necessity vanishing (being converted into liquid and gaseous products through the agency of bacteria), but we cannot regard this view as either proved or probable and consider that ulmins can be produced from any plant material of carbohydrate type. Judging from the nature of peat, ulmification is the main chemical process during the decay of plants and it proceeds further the older the deposit. Thus, while a young peat may yield only 10 or 20 per cent. of material soluble in alkalies, from an older peat as much as 70 or 80 per cent. can be extracted.

In a deposit of the age of coal, it cannot be expected that the materials of any of the three groups will remain unaltered. Spore exines and cuticular tissues may not be much changed, nor need the resins, but the cellulose that is not totally destroyed will in large part be converted, together with the more resistant lignin and part of the cell-contents, into the amorphous ulmins of group 3 (or products derived from them). There will also be material corresponding with group 2 (*a*), consisting of altered (but apparently not ulmified) woody tissues, such as compose many lignites and are recognizable in many bituminous coals. We have at present no knowledge as to what becomes of the non-ulmified portions of the cell contents. As they finally appear in the coal, cell-wall structures, group 2 (*a*), may not differ much chemically from the amorphous ulmins, but the materials of group 1 differ markedly.

Our knowledge of coal does not allow of these anticipations being thoroughly tested. We are, for example, only beginning to obtain evidence of the chemical relationships between the apparently well-preserved spore exines and cuticles of coal and those of the original plants. As regards the resins, it has been shown by White[5] that these can persist apparently unchanged in coals up to bituminous rank, but that in the older coals they show signs of having suffered alteration. It is possible, however, that resins persist without material alteration through-

[4] *Loc. cit.*

[5] U. S. Geol. Surv. *Prof. Paper* 85 (1914).

out the mass of many of the older bituminous coals, for there are occasional inclusions of undoubted resins that can readily be separated from them.

When we consider the contribution to coal of the alkali-soluble amorphous material that forms so large a part of recent deposits, such as peat, a decided difference is at once apparent. The proportion of material soluble in alkaline solutions progressively decreases in the older deposits, until from the higher rank bituminous coals and the anthracites little or none can be obtained. Although it has been suggested that the absence of soluble ulmins in the older fuels is due to the fact that their mode of formation was different from that of peat, it can be more simply accounted for by assuming a change in the character of the ulmins, through condensation, dehydration, and loss of carboxyl, resulting in their losing their "characteristic" solubility in alkaline solutions. This suggestion implies that the amorphous cementing material for the numerous plant structures in coal was originally a soluble ulmin, corresponding to the ulmins that surround and permeate the plant structures in peat. Moreover, its amount should be comparable with that of the soluble ulmins in the older peats.

Chemical evidence of this relationship is not difficult to find. Fischer and his co-workers have been able to demonstrate to some extent the presence of the same groupings and structures in peat ulmins, brown coals, and bituminous coals, and we have found that a close relationship in chemical structure exists between the peat ulmins and a characteristic amorphous portion (vitrain) of bituminous coal, and between the latter and the general ground mass of all portions of bituminous coal. Further evidence of the ulmic nature of much of the coal substance may be found in the "resolution" of coal by prolonged oxidation into soluble "ulmins" (oxidized ulmins) and plant entities in the manner described by Francis and Wheeler.[6]

Our comparison between peat and coal has concentrated on two substances that show remarkable physical resemblances; viz. dopplerite, from peat, and vitrain from banded bituminous coal. Dopplerite is essentially a homogeneous black jelly, of infrequent occurrence, found in layers at varying depths below the surface of peat bogs. Usually entirely free from plant structure, it sometimes exhibits a faint network of, apparently, cellular structure. From its composition, solubility in alkalis and general chemical behavior it must be regarded as an almost pure form of peat ulmin. To the majority of those who have studied it, its mode of occurrence has suggested that it was formed as a liquid or plastic mass. Several suggestions may be advanced to account for this especial and peculiar occurrence of a peat ulmin: (1) Chance precipita-

[6] Resolution of Coal by Oxidation; see p. 165.

tion (*e. g.*, by a solution of iron sulfate) of ulmins dissolved in alkaline solutions produced by the disintegration of rocks; (2) the formation of ulmins directly from solutions of amino-acids and carbohydrates produced by bacterial action from the accumulated vegetable matter, giving first water-soluble and then water-insoluble ulmins; and (3) interaction of the cellular tissue and the nitrogenous contents of the plant cells *in situ* (probably in general after partial decay) resulting when not quite complete in the network of cellular structure filled with jelly that is sometimes to be observed in dopplerite.[7]

The similarity of form and occurrence of dopplerite and vitrain will be evident. Chemically, the two substances also show certain similarities, with just those differences that would be expected from their different geological ages. The similarities appear in their products of destructive distillation. The tars from an Irish dopplerite and a Hamstead (Warwickshire) vitrain are of the same type, and the gaseous products, apart from a large and characteristic evolution of carbon dioxide from the younger ulmin, are almost identical, at all temperatures of distillation. The marked evolution of carbon dioxide (together with a large proportion of water) from the dopplerite indicates the presence in the molecule of carboxyl and hydroxyl groups that are easily split off and the differences in composition between the dopplerite and the vitrain can be accounted for entirely by the splitting off of these external groupings. Concomitant with the loss of these oxygenated groupings, we should expect to find a loss of solubility in alkaline solutions, but an increase in solubility in organic solvents, as the residue approximates more and more closely to a hydrocarbon structure. This is in fact observed.

We therefore consider that there are ample grounds for the conclusion that vitrain is similar to, though not identical with, dopplerite, and that it represents a more advanced stage in the process that has formed dopplerite from the decaying vegetation.

The proof of the close analogy between peat and coal, supported by the relationship found between dopplerite and vitrain, is completed by a demonstration of the identity of the amorphous material encrusting the plant structures in coal with that essentially free from plant entities, as in vitrain.

The four ingredients of banded bituminous coal—vitrain, clarain, durain, and fusain—show marked differences under the microscope. Vitrain is transparent and essentially free from plant structures;[8]

[7] Winter: *Gluckauf* (1922) 58, 1533.

[8] Though free from such structures as spore exines and cuticles many apparent vitrains show the forms of isolated or even generally distributed cellular tissues. These vitrains can be regarded as impure or incomplete. They were perhaps formed *in situ* from woody tissue that had not been entirely ulmified.

clarain shows numerous and varied structures in a transparent matrix; durain, a large variety of structures in an opaque granular matrix; and fusain consists almost entirely of blackened and thickened cellular tissues.

We have been able to trace a marked relationship chemically between these four ingredients, and particularly between vitrain, clarain, and durain, displaying itself in a regular gradation in their composition, in their susceptibility to the action of solvents and reagents, and in their response to heat treatment. Thus, the gaseous products of distillation were substantially identical in composition and varied in the same manner with the temperature of distillation, though the quantities obtained decreased in the vitrain, clarain, and durain in the ratio 1.0 :0.9 :0.7. The same ratio applied to the general "reactivity" of the banded ingredients of the coal. The explanation of this relationship lies in the fact that the ingredients are compounded of two distinct types of substances, the one "reactive," the other relatively "inert."

The "reactive" material appears to be of a similar nature in each ingredient, so that with the recognition of the essentially ulmic origin of the vitrain, the bulk of it can be considered as "reactive" and it follows that the "reactive" material of the remainder of the coal is also composed of altered (aged) ulmins, which must thus be present to the extent of 90 and 70 per cent., respectively, in the clarain and durain of the Hamstead coal. There seems no reason to doubt the presence in the Hamstead coal (and, by inference, in other bituminous coals) of altered ulmins to this large extent, in complete analogy with the presence of soluble ulmins in peat.

The question then remains as to the function in coal of the organized plant remains that form an apparently considerable part of clarain and durain. There are grounds (from a comparison of woody lignites with dopplerites) for the belief that certain of the plant structures, in particular the cellular tissues, may exist in coal in a form similar chemically to the ulmins. Otherwise, the plant entities must constitute what we have termed the "inert" material of coal.

DISCUSSION

David White, Washington, D. C.—The idea foreshadowed in the two preceding papers that vitrain is essentially ulmic or humic matter is here more clearly expressed. The plant structures present in it, and which appear as accidental or shadowy residues are, I believe, largely of a common composition as well as origin with the ulmic decomposition matter, both being of carbohydrate origin.

A. C. Fieldner, Pittsburgh, Pa.—Separation by hand of the bright and dull coal bands of several individual samples of banded coal, and chemical analysis and coking tests of these portions have shown rather

minor differences in chemical composition. It may be that, in American coals, the differences between bright and dull bands, or clarain and durain, are not so marked as in the English coals. From the similarity of the chemical analyses, one is led to believe that the greater percentage of the ground mass in both bright and dull coal is of similar composition—that is, a product of ulmic matter.

The principal difference between clarain and durain, or bright and dull coal, is in the coking properties. Typical bright coal, or anthraxylon, fuses completely, but durain, or attritus, does not fuse. Doctor Jeffrey's work suggests following through the transformation of wood into coal with a view to determining the particular stage at which the woody disintegration product takes on itself the properties of fusing and becoming plastic, as in coking coal.

Organic Sulfur Compounds in Coal

By J. Jolly* and R. V. Wheeler,† Sheffield, England

(New York Meeting, February, 1925)

This short note on the probable character of the organic sulfur compounds in coal can do no more than indicate lines of research. We have no new experimental work to describe, nothing comparable in value with the careful studies of American coals by Powell and Parr[1] and Yancey and Frazer.[2] A study of the manner in which sulfur compounds exist in British coals (and their behavior on heat treatment) is rendered increasingly necessary by the fact that the British reserves of good coking coals of reasonably low sulfur content are fast being depleted. We believe that it is essentially by a study of the modes of formation, occurrence, and decomposition of the various types of inorganic and organic sulfur compounds in coal that it will be possible, with hope of success, to attack the problem of purifying coals, otherwise eminently suitable for coking, from these objectionable ingredients.

Sulfur, so far as is at present known, does not normally occur in the free state in the coal conglomerate, but is chiefly distributed, irregularly, in three forms:

1. As primary constituents of the coal conglomerate, organic in nature and probably associated with those molecular complexes that have resulted from the degradation of the proteins of the plant tissues responsible for the formation of the coal mass. These constituents can be classed as "organic sulfur."

2. As metallic sulfides, *e.g.*, iron pyrites.

3. As metallic sulfates, *e.g.*, calcium sulfate and ferrous sulfate. (The occurrence of these compounds varies with the occurrence and degree of degradation of class 2.)

It is usually found that sulfur compounds of class 3, the metallic sulfates, are present in coal in small proportions only, amounting to about 1 or 1.5 per cent. of the total sulfur. The compounds in classes 1 and 2 are therefore of more importance. Class 1 alone will receive considera-

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[1] Univ. Ill. *Bull.* 111 (1919); synopsis published in *Trans.* (1920) 63, 674.

[2] Univ. Ill. *Bull.* 125 (1921).

tion in this paper, though, when considering the possible forms in which "organic sulfur" can be present in coal, it should be borne in mind that there may be a relationship between the occurrence of these organic complexes and that of the metallic sulfides, which may possibly also owe their presence in coal to the sulfur compounds originally present in the vegetation from which our coal measures were formed.

On this subject, we receive help from researches dealing with the sulfur contained in modern plants, more particularly from those relating to the proteins in cereals. The sulfur in plants resides mainly in the proteins contained in their seeds (in the germ and its associated food supply), while some proteins are transported through the phloem cells of the living plant tissues. Little is known regarding the latter, because of their transient existence, but botanists have obtained a fair amount of success in their endeavors to elucidate the problem of the structure of the sulfur complexes which are invariably present as an integral part of the seed organs.

Osborne[3] has investigated the properties of the proteins in a number of cereals and has shown that they differ, in different cereals, in their reactivity under direct chemical attack. For example, on boiling the different seed materials with a 30-per-cent. solution of lead acetate during several hours at a temperature of 165° C., some of the sulfur could be isolated as cystine while the residues contained varying quantities of more stable sulfur compounds. The sulfur isolated as cystine Osborne termed "loosely bound sulfur" and the more stable compounds "resistant sulfur." The proportions in which these are contained in cereals are indicated by the following data from his experiments:

Protein	Total Sulfur, Per Cent.	Loosely Bound Sulfur (Isolated as Cystine), Per Cent.	Total Sulfur as Loosely Bound, Per Cent.
Phaseolin, from the kidney bean	0.312	0.072	23
Edestin, from hemp seed	0.880	0.346	40
Glycinin, from the soy bean	0.710	0.320	46
Gliadin, from wheat	1.027	0.619	60

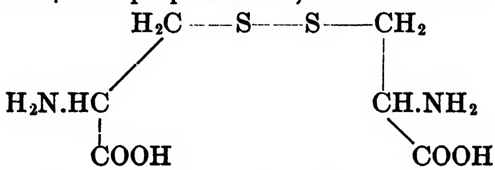
From the results of many experiments, Osborne concluded that, in general, a protein rich in sulfur was not of necessity rich also in those compounds that were acted upon by the reagents he used, and that there was evidence of at least two types of sulfur complexes of different degrees of reactivity.

It seems to be generally admitted that the degradation products of proteins are similar in character whether the proteins be of vegetable or animal origin. The work of Harris[4] on proteins of animal origin can

[3] *Jnl.* Amer. Chem. Soc. (1902) **24**, 140.
[4] *Proc.* Roy. Soc. (1922) B. **94**, 426.

therefore be drawn upon to supply evidence in support of Osborne's views. Harris found that 89 per cent. of the sulfur in serum albumen could be isolated as cystine, the remainder being stable, while from ovalbumen only 14 per cent. could be isolated as cystine. He found, moreover, that the sulfur in proteins only becomes reactive under certain conditions of experiment and in all the organic compounds he investigated a proportion (which varied with the compound) of the sulfur existed in a very stable form. The isolation of the maximum quantity of organic sulfur was only possible under optimum conditions of experiment, which varied with each compound.

The oxidation of cystine, which can be isolated as one of a group of dehydration products of proteins, has been studied[5] and it has been found that its reactivity (and that of its reduction product cystein) can be controlled in a suggestive manner. Cystine is a diamino acid, the disulfide of α-amino β-thio propionic acid, of the formula:



while its reduction product, cystein, is a mercaptan. The oxidation of these compounds can be accelerated by the presence of iron in minute quantities, while if a cyanide is also present, as an additional catalyst, the reaction is still further accelerated. For example, the presence of as little iron as M/10,000 was found to double the rate of oxidation. The oxidation process appears to be intra-molecular and the iron to act as an oxygen carrier, being loosely held in combination until the reaction is complete. Another important observation is that the rate of oxidation of cystine is greatly reduced by the presence of a solution of sodium, potassium, or calcium chloride of 4 mol. strength.

Baumann and Goldmann[6] have also studied the behavior of cystine toward reagents and have shown that it is remarkably inert toward many, while with all time of contact is an important factor. For example, in two experiments in which cystine was boiled with a 10-per-cent. sodium-hydroxide and lead-acetate solution only 68 per cent. of its total sulfur was yielded as sulfide after 9 hours treatment and 83 per cent. after 33 hours.

Similarly, experiments by Schultz[7] on the treatment of cystine with a 30 per cent. solution of sodium hydroxide in the presence of zinc and oxide of bismuth, showed that 53 per cent. of the sulfur was obtained as sulfide after 10 hours boiling and 53.7 per cent. after 25 hours.

[5] Matthews and Walker, *Jnl.* Biol. Chem. (1908) **6**, 289.

[6] *Ztschr. physiol. Chem.* (1888) **12**, 257.

[7] *Ztschr. physiol. Chem.* (1898) **25**, 16.

There is thus ample evidence regarding the existence, in the naturally occurring organic sulfur compounds, of groupings containing sulfur that are not readily decomposed and are comparatively inactive; while other groupings yield their sulfur fairly readily, probably as hydrogen sulfide, on treatment with reagents. It would seem also, from the general observations made by different experimenters, that a necessary preliminary to the resolution of the sulfur-containing complexes in proteins, whereby the comparatively unstable compounds are formed, is their partial oxidation.

This evidence of the stability, in favorable circumstances, of certain of the protein sulfur compounds in living plants suggests that some of the sulfur compounds that were present associated with plant entities that are still recognizable in, and can be isolated from, coal may not have been considerably changed during the coal-forming process, and may exist in coal today in a form but little modified. Certainly those parts of plants, cuticles and spore exines, that can be isolated from bituminous coals do not differ chemically to a great degree from the cuticles and spore exines of modern plants. The visible plant entities do not, however, often form a considerable part of the coal mass, and there is no reliable evidence that organic sulfur may be concentrated in them. On the other hand, it is presumed that the formation of part of the ulmic ground mass of coal has been in the first instance by the condensation together, to form amino ulmins, of the carbohydrates and amino acids of the decaying plants. If cystine were involved in such a condensation, sulfur-containing organic compounds might be dispersed throughout the coal-forming mass.

This latter appears to us the more likely hypothesis. It can be elaborated to explain the existence in coal (so evident on its destructive distillation) of varying proportions of organic sulfur compounds of different degrees of stability. As a generalization, it may be stated that vegetable tissues when undergoing decay suffer progressive oxidation. The oxidation is no doubt sometimes checked, because of temporary adverse conditions, and may proceed again; or it may be permanently stopped according to the particular environment of the decaying materials. We thus have the conditions necessary to promote the resolution of the sulfur-containing complexes in the proteins with the production of a proportion, dependent on the environment, of comparatively unstable compounds. Further, by analogy with the behavior of cystine under the action of catalysts, it can be understood that the action of ferruginous waters on the vegetable material undergoing decay would be to hasten the resolution of the proteins while the action of alkaline waters would be to preserve them.

Here our conjectures cease. The experimental work we have undertaken to test them is designed to estimate the proportions of relatively

stable and unstable organic sulfur compounds, which undoubtedly exist in coal and, ultimately, to determine their character.

DISCUSSION

S. W. PARR, Urbana, Ill.—The paper works back to the organic compounds and their probable types through the medium of sulfur, but our practical interest does not lead us in that direction. We want to know how much of the sulfur is mineral and how much is organic? Fortunately the organic sulfur is not easily dissolved and the mineral sulfur is. By a purely empirical method, dilute ordinary hydrochloric acid, if given time enough, will dissolve the mineral sulfur and not touch the organic sulfur. The separation can be hastened considerably by warming the solution a little. In the coking of this material, it does not make any difference whether the sulfur is in the mineral or in the organic form.

Selective Combustion in Coal

By F. S. Sinnatt,* East Greenwich, England

(New York Meeting, February, 1925)

This paper is the outcome of an extended investigation carried out in association with Dr. L. Slater. The inquiry had been continued in various directions and a number of results are quoted from an investigation recently completed by S. H. Jenkins. In projecting the work some five years ago, the author had in view a general attack on the problem of the spontaneous combustion of coal from an angle that had received little attention. The basic idea was to obtain a "slow motion study" of the active combustion of coal. This included an examination of the conditions prevailing in a mass of coal at the moment when active combustion ceases. It was thought that, if the factors governing the extinction of combustion in coal could be definitely established, it might offer an explanation of the manner in which the spontaneous combustion of coal originates.

The inquiry arose from a detailed study of the properties of fusain that the author began in 1918. Fusain seemed to possess characteristics quite distinct from the coal with which it was associated, for if it were collected into a heap and one portion were heated by a small flame the combustion would traverse the whole mass. This combustion was not accompanied by smoke and passed slowly through the heap of material. Later, it was found that coals, including anthracites, would behave in a similar manner provided they were in the form of powder and that the particles were smaller than a certain size. The limiting size of particles is a definite characteristic of the coals investigated. In view of the fact that fusain exists with coal in a state that enables it to undergo this particular form of combustion, it must be assumed, sometimes, to play a definite part in the spontaneous combustion of coal in the goaf (waste).

Tables 1 and 2 contain the analyses of samples of dust collected from a mine and from a dust collector. Some idea of the degree of fineness of the particles of fusain may be obtained from a study of the analyses of the dust from the dust collector; 80 per cent. of the dust would pass through a 200-mesh screen while the fusain was concentrated in the finest dust. The material that passed through a 90-mesh screen contained 54 per cent. of fusain while that between a 30- and a 90-mesh only con-

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tained 13 per cent. All the samples would propagate a zone of combustion when one portion of a heap was heated with a small flame.

TABLE 1.—*Amount of Fusain Found in Mine Dust*

Description	Sample No. 1, Per Cent.	Sample No. 2, Per Cent.	Sample No. 3, Per Cent.	Sample No. 4, Per Cent.
Moisture	1.3	0.9	1.4	1.4
Ash	28.7	10.1	23.2	19.2
Volatile matter	21.8	22.5	25.0	25.4
Volatile matter less moisture	20.5	21.6	23.6	24.0
Coke	78.2	77.5	75.0	74.6
Fixed carbon	49.5	67.4	51.8	55.4
Fusain	25	47	16	21

TABLE 2.—*Examination of Dust from Dust-collector*

(Average sample; proximate analysis)

	Per Cent.
Moisture	1.2
Ash	9.1
Volatile matter	22.6
Volatile matter less moisture	21.4
Coke	77.4
Fixed carbon	68.3
Fusain	49

QUANTITATIVE SIEVING TEST OF THE DUST SHOWED

Above 30-mesh	0.0
30- to 60-mesh	1.5
60- to 90-mesh	3.0
90- to 200-mesh	15.5
Through 200-mesh	80.0

ANALYSES OF FRACTIONS

30- to 90-mesh	Per Cent.	Through 90-mesh	Per Cent.
Moisture	2.1	Moisture	1.2
Ash	7.0	Ash	9.6
Volatile matter	31.3	Volatile matter	21.4
Volatile matter less moisture	29.2	Volatile matter less moisture	20.2
Coke	68.7	Coke	78.6
Fixed carbon	61.7	Fixed carbon	69.0
Fusain	13	Fusain	54

It may be mentioned that the seams from which these dusts were produced only contained about 1.5 per cent. of fusain.

PROPAGATION OF ZONE OF COMBUSTION

The experiments on the propagation of a zone of combustion were carried out in the following manner: Cones of pulverized coal of standard

size and with uniform packing of the particles were formed by filling a glass funnel with coal and inverting it upon a silica plate (Fig. 1). The coal dust was allowed to fall into the funnel from an orifice placed at a constant level above it, and the excess of coal above the edge of the funnel was removed by means of a broad sharp blade.

The apex of the cone was heated momentarily with a small flame. The combustion thus initiated develops into a zone which passes regularly throughout the mass, provided the conditions mentioned later are satisfied. The combustion is characterized by two well-defined stages: First the color of the coal changes from brown to black, and this is succeeded by a zone in which rapid combustion occurs. The fact that combustion is taking place is not always apparent, as the temperature attained is only sufficient to produce a dull red glow. That the first stage of the combustion is clearly defined was proved by experiments in

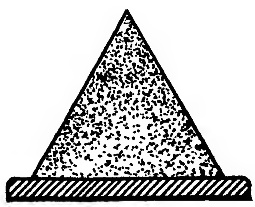

FIG. 1.—PROPAGATION OF ZONE OF COMBUSTION.

which the combustion was allowed to proceed under similar conditions but in a limited supply of air. The combustion is accompanied by little smoke and the odor evolved is similar to that noticed in the early stages of a gob fire.

When the combustion has started in a heap of coal dust, the area may spread until every part, except the portion in contact with the plate on which the coal is standing, has been oxidized. If the combustion proceeds vigorously, some part of the coal may be completely oxidized and ash alone may remain. If the combustion takes place slowly, either because the particles are large or because the supply of air is limited, a cone-like residue is formed. If the residue from the combustion in a restricted supply of air is allowed to cool and one portion of the mass is again heated, a zone of combustion will again travel throughout the heap. This experiment has been repeated four times with one charge of coal; only part of the oxidizable material in the heap is affected during each combustion. The explanation that suggests itself is that each oxidation is a differential one. It is presumed that with more refined experimental methods the number of combustions might be increased. The experiment disproves the belief that when a gob fire has occurred in a certain mass of coal, or in one part of a mine, a second gob fire cannot take place in the same coal or in the same region. There appears to be

no reason why a gob fire should not occur a number of times in the same quantity of coal.

The zone of oxidation may not spread uniformly throughout the heap, but may follow a well-defined path and leave the remainder of the coal nearly unaffected. The exact conditions that are favorable to the propagation of a zone of combustion in a particular region cannot be defined accurately at present, but absence of uniformity in the packing of the particles has a marked influence. It is not possible to assume that the combustion follows the path of most open packing, although experiments in which the powdered coal was placed under pressure have shown that the propagation of the zone was then retarded or entirely prevented.

The behavior of the coal during the period of active combustion, *i.e.*, as the zone of combustion is passing, varies not only with the type of coal and the oxygen available, but with the size of the particles. When the oxidation is allowed to proceed in the presence of an excess of air, the mass of coal decreases in volume if the particles are below a critical size. When larger particles are associated with the fine coal, the oxidation is accompanied by a slight increase in the volume of the mass if the coal is a caking variety. It is found that a portion of the coal may undergo more complete oxidation while the residue is partly oxidized and carbonized. The carbonized particles are converted into minute spheres of coke-like material. When the heap has a surface that is vertical or at an angle greater than the angle of rest of the coke-like product, the spheres of the latter will roll from the zone of combustion and may then be collected at the base of the heap. With anthracites, which are non-caking and non-swelling, there is a slight decrease in the size of the heap during oxidation.

Although the oxidation may be proceeding along a definite path, the change in volume produced in the mass at the moment of active oxidation may be such as to prevent the zone of combustion proceeding farther in a particular direction. Only caking coals have been examined in this connection.

TABLE 3.—*Limiting Size of Particles of Three Coals*

Anthracite		Ravine		Arley	
Figure of Fineness	Oxidation	Figure of Fineness	Oxidation	Figure of Fineness	Oxidation
1.1142	Complete	1.350	Complete	1.370	Complete
1.1501	Incomplete	1.385	Complete	1.1388	Complete
1.1667	No combustion	1.1497	Complete	1.405	Complete
		1.563	Complete	1.455	Complete
		1.1655	No combustion	1.489	Complete
				1.602	Complete
				1.684	No combustion

Table 4.—*Values Obtained in the Screening Tests and Analyses of the Coals*

Hours Grinding	Per Cent. on 90-mesh	Per Cent. on 120-mesh	Per Cent. on 150-mesh	Per Cent. on 200-mesh	Per Cent. through 200-mesh	Figure of Fineness
			Ravine			
1	32.14	8.36	12.47	7.42	39.61	1.2157
2	23.50	8.44	15.07	9.75	43.30	1.2138
3	24.07	9.87	16.60	7.65	41.81	1.2118
4	15.45	11.88	14.43	8.86	49.39	1.1983
5	6.94	8.99	13.65	8.25	62.24	1.1859
7	1.61	3.09	11.87	9.53	73.90	1.1655
9	0.58	0.76	3.93	4.63	90.13	1.1563
13	0.20	0.46	3.34	2.67	93.32	1.1497
16	0.91	0.48	1.72	2.43	94.45	1.1385
20	1.56	1.06	2.03	1.28	94.2	1.1350
			Arley			
1	25.28	8.30	12.71	7.33	46.25	1.2155
2	20.28	8.62	14.36	6.02	50.48	1.2090
3	5.63	6.12	16.26	5.02	68.00	1.1801
4	2.05	2.96	11.07	5.78	78.40	1.1684
5	1.07	1.40	6.73	7.70	83.20	1.1602
7	1.45	1.50	5.05	1.94	90.00	1.1489
9	1.37	1.45	2.96	1.75	92.40	1.1455
13	2.46	1.55	3.68	2.00	90.40	1.1405
16	2.78	2.40	4.96	2.70	87.20	1.1318
20	3.4	1.48	5.20	4.20	83.60	1.1370
			Mountain Mine			
1	24.09	10.62	14.68	6.67	43.94	1.2214
2	20.92	8.97	17.15	7.81	45.15	1.2082
3	7.25	9.99	15.40	7.72	59.63	1.1888
4	2.56	4.16	12.18	10.63	70.48	1.1776
5	1.43	2.73	11.11	5.94	78.79	1.1685
7	1.37	1.16	5.44	7.65	84.38	1.1605
9	1.11	1.24	4.11	6.44	86.96	1.1548
13	1.89	1.61	3.55	3.51	89.48	1.1469
16	2.55	2.05	4.29	4.16	86.94	1.1431
20	3.36	1.91	6.29	4.32	84.14	1.1413

Proximate Analyses	Mountain Mine	Arley Mine	Ravine Mine
Moisture	2.73	1.93	2.42
Ash	3.52	3.23	4.05
Volatile matter	26.46	35.34	36.56
Volatile matter less moisture	23.73	33.42	34.14
Coke	73.54	64.66	63.44
Fixed carbon	70.62	61.43	59.39
Ultimate Analyses			
Carbon	81.94	82.32	78.42
Hydrogen	5.28	5.51	5.24
Nitrogen	1.16	1.54	1.50
Sulfur	1.61	1.45	2.28
Ash	3.62	3.29	4.15
Oxygen (by difference)	6.39	5.89	8.41

Table 3 records the limiting size of particles for three coals—Arley, Ravine, and an anthracite. The fineness was determined by an exhaustive screening test and is expressed in the terms of the figure of fineness.[1]

With Ravine coal, all samples in a finer state of division than that corresponding with a figure of fineness 1.1655 would ignite readily and the combustion would proceed throughout the mass of coal dust. With the Arley coal, the oxidation would proceed over a much wider range, for all dusts finer than indicated by a figure of fineness 1.1684 would ignite and burn completely. Anthracite obtained by grinding during 20 hours (figure of fineness 1.1142; 98 per cent. through 200-mesh) would ignite and the combustion would proceed until the oxidation was complete, but specimens coarser than this could not be made to burn completely. These results indicate that two factors predominate: the character of the coal; and the fineness of division of the coal.

The two bituminous coals show that a sharply defined value exists for the critical degree of fineness necessary to enable the combustion to proceed and indicate that the ratio of surface exposed to the weight of the particles is a factor in deciding whether the oxidation of the coal will proceed autogenously under the conditions postulated. It would appear that experiments on the oxidation of coal by earlier investigators may have yielded erratic results from the fact that the particles of individual specimens of the coal may have been above or below the critical degree of fineness.

Rate of Propagation of a Zone of Combustion

It was thought that the rate of oxidation of the dusts might offer means of determining the liability of a coal to spontaneous combustion, so attempts were made to obtain a measure of the rate at which combustion was occurring. The method adopted was to allow the dust to oxidize in a narrow "train" and to note the time required for the combustion to pass from point to point.

A metal trough, 5 in. long, ¼ in. in width, D-shaped in cross section and closed at the ends, was used to make the "train" of coal dust. The trough was held in position horizontally beneath an orifice and dust was run into it, in a thin stream, until it was filled and overflowing at the sides; the excess was then removed by means of a sharp blade until the coal was level with the edges of the trough. A thin silica plate 7 by 1 in., graduated by a series of lines 1 in. apart at right angles to the longer dimension of the plate, was placed on the trough. The whole was then inverted and placed on a firm base, and the metal trough carefully removed so as to avoid any displacement of the coal dust. A heap, or "train," of coal dust remained on the plate 5 in. long, the same height

[1] *Fuel in Sci. & Prac.* (1923) **2**, 142.

throughout its length, and uniformly packed. The apparatus was protected from drafts. The trough and plate with a train of coal in position are shown in Fig. 2.

The train of coal was ignited at one end by a small flame; the oxidation was found to proceed at a perfectly uniform rate to the opposite end of the train, leaving a residue of coke or of ash according to the method of treatment.

The front of the zone of combustion could be readily followed by observing the sharp color change in the coal dust from brown to black. The time taken for the oxidation to proceed over a definite length of 4 in. of train was determined. The results obtained are given in Table 5.

TABLE 5.—*Rate of Propagation of Combustion*

Coal	Hours of Grinding	Figure of Fineness	Time Occupied for Combustion over 4 In., Minutes
Arley	36	1.1320	24
	20	1.1370	24
	16	1.1338	24
	13	1.1405	24
	9	1.1455	28½
	7	1.1489	31
	5	1.1602	36½
	4	1.1684	42½
		No combustion with larger particles	
Mountain mine	20	1.1413	24
	16	1.1431	26½
	13	1.1469	29
	9	1.1548	36
		No combustion with larger particles	
Ravine	20	1.1350	22½
	16	1.1385	28
	13	1.1497	34
	9	1.1563	38
	7	1.1655	48
Anthracite		Propagation of combustion along train did not take place even with finest powders.	

The most finely ground specimens of Arley and Mountain Mine coal required the same period of time (24 min.) to burn over a length of 4 in. of the train, while the Ravine coal for a similar degree of fineness only required 22½ min. This indicates a marked readiness on the part of the latter coal to oxidize in the air; a significant observation in view of

the fact that the Ravine coal is liable to undergo spontaneous heating in the goaf.

It will be observed that the results correspond, in general, with those obtained when conical heaps were used. Both the Arley and the Ravine coal dusts failed to propagate a zone of combustion along the train when the sizes of the particles were similar to those that failed to allow of propagation in the heaps; while with the Mountain Mine coal progressive combustion of the particles below the figure of fineness 1.1548 did not occur.

Attention must be called to the great difference in the time required for the propagation with alterations in the degree of fineness of the dusts.

Within the limits of the experiments herein recorded, Arley coal required from 24 min. to 42½ min. for the combustion to travel 4 in.,

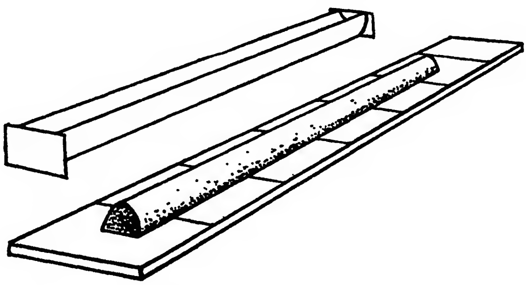

FIG. 2.—DETERMINING RATE OF PROPAGATION OF A ZONE OF COMBUSTION.

according to the degree of fineness of the particles. In view of this variation, it would not appear possible to standardize the present method of examining the liability of a coal to spontaneous combustion unless the dust is in a state of division approaching the limiting degree of fineness as indicated by the "figure of fineness." As the limit of fineness is reached, the rate of combustion along a train assumes a limiting value; and this limiting value for the rate of combustion may afford a measure of the liability of the coal to undergo spontaneous combustion.

The limiting value for the rate of combustion appears to have been reached with one coal only, the Arley, which shows the same rate of combustion for samples ground for 16, 20, and 36 hours, respectively. Mountain Mine and Ravine coals do not exhibit this approach to a limit. Although the combustion proceeds in the train of Mountain Mine coal dust within narrower limits of fineness of the dust than obtains with either Ravine or Arley coals, with samples of comparable fineness the rate of combustion with the Mountain Mine coal is greater than with either of the other two coals. The fact that the limiting value for the rate of combustion is suddenly attained with the Arley coal indicates the possibility of there being an equally abrupt approach to the maximum rate of combustion with the other coals as the state of division of the

dust particles is increased; and it is necessary that before anything definite is stated with regard to this particular point a larger number of coals that have been ground during an extended period should be tested.

Modifying Influence of Various Compounds on Rate of Combustion

It was considered desirable to examine the modifying influence of the addition of various compounds on the rate of combustion of finely powdered coal under the conditions of the present experiments. As a preliminary experiment, the influence of the presence of finely divided calcium carbonate was investigated. Pure calcium carbonate that had passed through a 150-mesh sieve was intimately mixed in various proportions with Arley coal (figure of fineness 1.1489). These mixtures were formed into trains and the rates of combustion determined in the manner previously described. The results obtained are given in Table 6.

Table 6.—*Combustion Rate of Coal and Calcium Carbonate Mixtures*

Coal, Per Cent.	Calcium Carbonate, Per Cent.	Combustion Time for 4 In., Minutes
100	0	31
90	10	30½
80	20	31
70	30	31

It will be observed that increased proportions of calcium carbonate failed to retard the rate of combustion; it required the addition of 70 per cent. of calcium carbonate to prevent entirely the propagation of a zone of combustion.

It was considered of interest to examine the effect of adding finely pulverized rock dust to the coal. Mixtures were made of various proportions of pulverized shale, which had passed through a 200-mesh sieve, and Arley coal of the figure of fineness 1.1370. It was found that the limiting quantity of stone dust in admixture with the coal dust that would just permit of combustion passing through the heap was 52 per cent. With a greater percentage, the mixture failed to ignite; while with lower percentages oxidation proceeded regularly throughout the train of mixture.

The possible catalytic effect of the presence of small amounts of ankerites containing manganese and ferrous salts was now examined. For this purpose, admixtures were made with Arley coal of a fineness of 1.1684 (figure of fineness). Coal dust of this size has a very slow rate of burning and was chosen because any increase in the rate of combustion due to catalytic action would be more readily observed. The time

required for the combustion to travel in the pure coal dust over a length of 4 in. of train was 42½ min. When small quantities of manganese and ferrous salts were added the results were:

	Minutes
1 per cent. manganese carbonate	42
1 per cent. ferrous sulfate	42½
1 per cent. ankerites from Arley coal	42½

There is apparently a slightly increased rate of combustion in the mixture containing manganese carbonate, but a variation of ½ min. in the measurement of the time is within the range of experimental error.

Temperature Recorded During Combustion

A platinum, platinum-rhodium thermocouple was introduced into a cone of coal dust in the manner shown in Fig. 3, the point of the couple being fixed centrally and ½ in. from the apex.[2] The apex of the cone was ignited, and a record of the temperature was made at 1-min. intervals. The results when using anthracite dust are given in Table 7. Only the values at 5-min. intervals are quoted for the sake of brevity.

Table 7.—*Combustion Temperature of Anthracite*

Time, Minutes	Degrees C.	Time, Minutes	Degrees C.
0	35	25	580
5	150	26	585
10	410	30	560
15	520	35	420
20	550		

Similar results were obtained with other coals, thus: Arley having a figure of fineness of 1.1370, the temperature reached 485° C. and remained stationary for 2 min. then rose to a maximum of 510° C. Ravine having a figure of fineness of 1.1350, had a gradual rise in temperature to 480° C., where it remained stationary for 2 min. then rose to a maximum of 540° C. Mountain Mine, having a figure of fineness of 1.1413, had a gradual rise to 450° C., where it remained stationary for 2 min. then rose to 510° C. maximum.

In each instance a maximum temperature is recorded varying from 510° to 585° C., and in the combustion of bituminous coals two distinct stages can be recognized marked by a pause in the rise of temperature. No stationary intermediate temperature could be detected with anthracite, but the rate of increase of the temperature became slower between 520° and 550° C. The fact that a first and second maximum are observed lends some support to the theory that a dual oxidation is proceeding.

[2] The glass funnel shown was not used in this series of experiments.

It is apparent that, other factors remaining constant, the main consideration which decides the oxidation of the coal is the rate at which the oxygen is able to react with the organic substances. Certain of the factors have already been discussed, and it is now proposed to consider the effect of variations in the oxygen supply.

Experiments were carried out with a cone of coal (Arley coal, figure of fineness 1.1370). The air was controlled by means of a funnel which was placed over the cone of coal as shown in Fig. 3. This funnel normally fitted closely to the glass plate upon which the cone of coal rested, and the air supply could be controlled by raising it above the glass plate. The height of the funnel from the glass plate was regulated by interposing between the edge of the funnel and the plate different numbers of very thin glass micro-cover slips. In the experiments to be described,

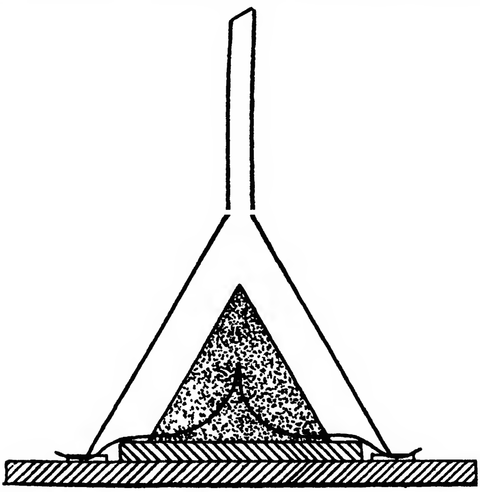

FIG. 3.—DETERMINING TEMPERATURE DURING COMBUSTION.

the coal dust was placed in position upon the glass plate in the manner already explained; the apex of the cone of coal was ignited, and the outer funnel placed in position resting over the cone of coal and maintained the distance of one cover-slip thickness from the glass plate. Thirty seconds after placing the funnel in position, the smoke that had been given off from the tip of the cone on first ignition ceased to be evolved. Moisture was deposited upon the inner surface of the funnel, and the oxidation spread regularly to the base of the heap, as could be detected by the change in color of the coal. The maximum temperature observed during the combustion was 280° C. The gases issuing from the stem of the funnel possessed a characteristic odor, apparently due to the presence of acetone. When the combustion had spread to the base of the heap, the funnel was removed and the heap of coal scattered upon the glass plate. Vigorous combustion immediately took place over the scattered

surface, various points reaching a temperature of 800° C. In a second experiment, combustion spread throughout the coal and again reached a temperature of 280° C., when further oxidation ceased. After the heap had assumed the normal room temperature, the funnel was removed and the heap cut into sections and examined. At no point could complete combustion resulting in the production of ash be observed. This is a distinctly different result from that obtained when the coal was allowed to burn in an excess of air. It would appear that with bituminous coals a preliminary oxidation occurs in which some very readily oxidizable constituent actively reacts with a comparatively limited supply of air.

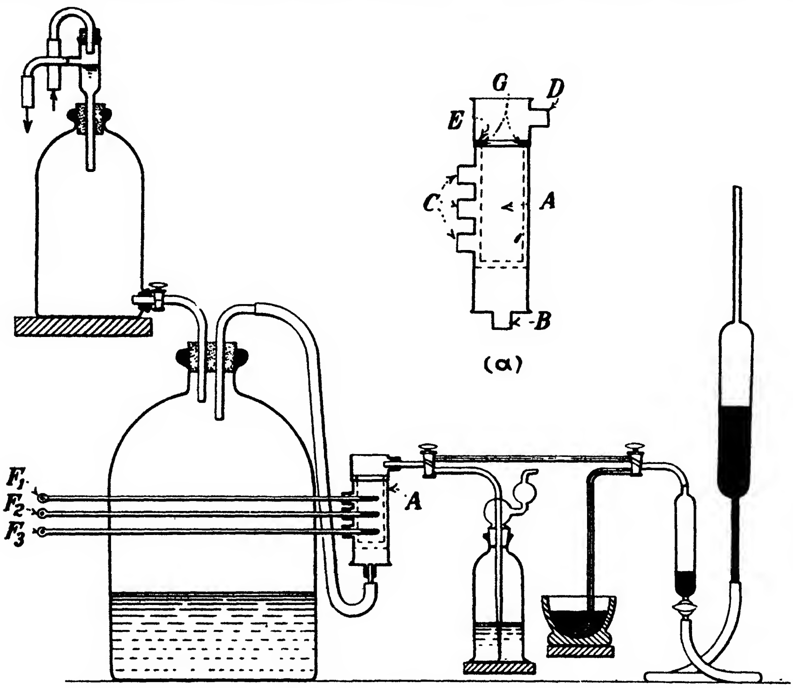

FIG. 4.—APPARATUS FOR CONTROLLED OXIDATION OF COAL.

Further tests were performed with the same apparatus supplying increasing volumes of air to the coal, by inserting two or more glass micro-cover slips between the funnel and the glass plate. It was found that the combustion could be modified until, with an excess of air, the coal oxidized completely.

Investigation suggested a container which allowed the oxidation to proceed as in the small conical heaps but in a controlled manner. A sectional diagram of this container is shown at (*a*) Fig. 4. It consists of a thin metal cylinder *A*, 5½ in. long, provided with a close-fitting lid and having an outlet at *B* and three short tubes at *C* placed vertically below

one another and 1 in. apart. The outlet from the lid is at *D*. A thin metal collar *E* is soldered on the inside of the cylinder *A* and to this is soldered a cylinder made from 100-mesh gauze, which is ⅛ in. smaller in diameter than *A* and 4 in. long. The gauze cylinder is pierced with holes cut to fit the thermometers *F* that pass through the side tubes *C*. A disk of 100-mesh gauze is soldered inside the cylinder *A*, in order to distribute evenly the air supplied. The general arrangement of the apparatus for carrying out an experiment is shown in Fig. 4, and needs no description.

An experiment was carried out in the following manner. Three thermometers *F* were inserted through the side tubes *C*, and held in rubber stoppers so that the bulbs were centrally placed along the axis of the gauze cage. Coal dust was gently poured into the cage from an orifice placed at a definite height above the top of the cylinder *A* until the gauze container was filled to the height *G*. A supply of air (at a definite rate) was passed through the inlet, and the tip of the cone of coal above the level *G* was ignited by means of a small gas flame. The lid was placed in position and the joint made gas-tight. The temperatures recorded by the thermometers were noted at 5-min. intervals; the results are given in Tables 8 to 11. (To simplify the tables only essential readings are quoted.)

It will be observed that in each experiment the thermometers in turn indicated a maximum. When an experiment was completed the thermometers were withdrawn, the product remaining in the gauze cage removed and examined as in the previous series of experiments. The

TABLE 8.—*Rate of Air Supply* 4412 *Cubic Centimeters per Hour*

Time	Thermometer Readings, Degrees C.		
	F_1	F_2	F_3
3:0	35	24	22
3:15	114	27	24
3:20	128	29	25
3:25	134 (max.)	31	27
3:30	132	32	27
4:0	74	43	29
4:15	57	97	32
4:20	50	105	34
4:25	46	111 (max.)	35
4:55	36	66	100
5:0	37	63	112
5:05	36	62	114
5:10	36	55	132 (max.)
5:15	35	53	115
6:30	22	22	22

TABLE 9.—*Rate of Air Supply 4491 Cubic Centimeters per Hour*

Time	Thermometer Readings, Degrees C.		
	F_1	F_2	F_3
3:45	22	20	20
3:55	86	24	23
4:05	164	31	27
4:10	167 (max.)	34	29
4:45	72	113	35
5:0	63	130	37
5:10	53	131 (max.)	38
5:30	41	79	92
5:45	38	66	132
5:55	39	59	148 (max.)
6:30	37	43	103
7:10	18	18	23

TABLE 10.—*Rate of Air Supply 6000 Cubic Centimeters per Hour*

Time	Thermometer Readings, Degrees C.		
	F_1	F_2	F_3
2:05	26	21	22
2:30	143	29	28
2:40	182 (max.)	33	31
	101	76	37
	94	99	38
3:15	85	130	40
3:25	70	152 (max.)	43
4:0	48	78	149
4:10	48	68	161 (max.)
4:30	44	50	140
5:0	41	44	88
5:15	40	94	58
6:0	38	47	109
6:15	38	47	95
6:30	36	40	48

whole of the product occupying the container had changed in color from brown to black, indicating that the wave of oxidation had in its progress completely enveloped the thermometer bulbs (except in one experiment), so that the temperatures recorded were those in the mass of the oxidizing coal and were not due to the passage of the zone of oxidation near to the thermometer bulbs. The exception is indicated by the maximum shown by F_2 in Table 11, where subsequent examination showed the bulb of the thermometer to have been just to one side of the path of the oxidation.

TABLE 11.—*Rate of Air Supply 6340 Cubic Centimeters per Hour*

Time	Thermometer Readings, Degrees C.		
	F_1	F_2	F_3
2:45	28	22	23
3:0	139	29	27
3:15	234 (max.)	37	32
3:30	127	62	37
3:45	90	150	41
4:05	74	174 (max.)	45
4:15	61	150	55
4:30	54	106	141
4:30	51	84	227 (max.)
5:05	50	61	142

Fig. 5 shows graphically the variations in temperature as the oxidation passed through the coal in the experiment, the results of which are given in Table 9.

The experiments of which the results are given were carried out with increasing volumes of air; it will be noted that, in general, increasing

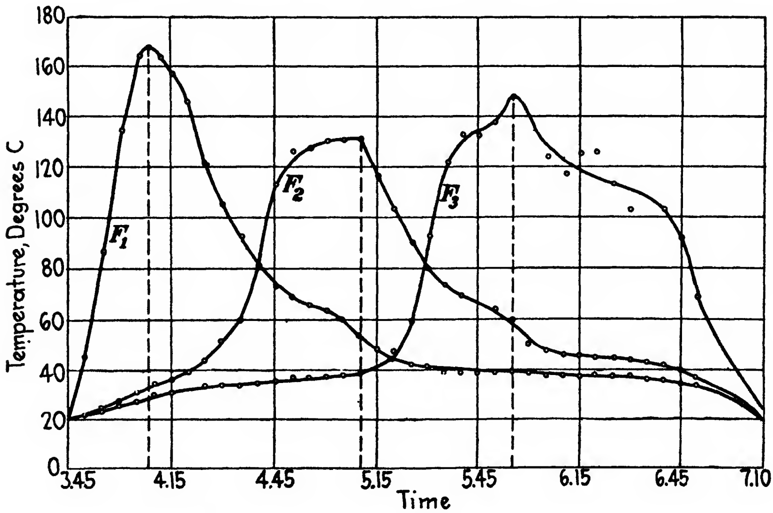

FIG. 5.—VARIATIONS IN TEMPERATURE DURING OXIDATION.

rates of air supply produce increasing temperatures during oxidation, and that between the range of supply of 4400 to 6340 c. c. per hr., the oxidation will pass through the mass maintaining approximately the same temperature throughout. If the rate of supply of the air falls below 4400 c. c. per hr., the initial oxidation induced at the tip of the cone of coal would not always proceed through the mass. Five experiments were attempted with an air supply at this rate; of these, four

failed to propagate the oxidation and one gave the results shown in Table 8, which records the lowest temperature at which the propagation has been observed to take place. A rate of supply of 6340 c. c. per hr. tended to produce very vigorous combustion when the wave of oxidation had reached the inlet end of the container. In this experiment, between passing the third thermometer F_3 (Table 11) and reaching the end of the column of coal the rate of oxidation would appear to have increased.

The slow rate of travel of the wave of oxidation through the coal is noteworthy. The time between successive maxima, as indicated by the thermometers, varies between 60 and 40 min.

The possibility of the development of this form of low-temperature slow oxidation into active combustion was illustrated by two experiments, in which the slow oxidation was produced at a temperature of 160° by a repetition of the experiment recorded in Table 9. The oxidation was allowed to proceed for 10 min. after the first thermometer F_1 had indicated a maximum of 160°; the air supply was then increased to 8000 c. c. per hr. After a lapse of 5 min., thermometers F_1 and F_2 indicated a very rapid rise of temperature beyond 360° C. and the air supply was stopped to check the complete inflammation of the coal.

A number of laboratory experiments have been carried out in which coal has been heated externally while a current of air is passed through. Determinations have been made of the temperature developed by a thermometer inserted at one point in the coal. Such a determination does not necessarily give the temperature of the coal. It is clear from the work of Winmill and Graham that coal may readily oxidize under certain conditions to produce temperatures of approximately 130° C. The work described here shows that once this temperature is achieved rapid oxidation may pass through the coal along a very irregular path and give quite erroneous figures for the temperatures in the mass.

Again, in considering the sources of underground heatings it would appear that oxidation once initiated in the fine material in the goaf is capable of traveling in a haphazard fashion at the rate of 2 ft. in 24 hr., and of developing into active combustion when the oxygen supply is sufficient. It is doubtful if the presence of large proportions of stone dust is capable of arresting the travel of such oxidation.

The character of the oxidations that have been described suggests a method for the determination of the temperature which a sample of coal must attain before the oxidation can pass rapidly into active combustion or can propagate through the mass in the absence of sufficient air. The conditions existing at this lower limiting temperature are such that the heat produced in the one layer of coal is enough to permit the next layer to be heated above that temperature at which the heat produced by oxidation can propagate to the next layer. If the amount of heat lost through radiation and convection to the outgoing

air and to the apparatus is so great that this temperature is not achieved, the oxidation will cease and the coal will return to normal temperature.

The determination of this lower limiting temperature was attempted in the following way. In the apparatus that has already been described, coal dust was ignited in an air supply of 5000 c. c. per hr.; this is sufficient to insure the development of a temperature of approximately 170° C. in the oxidation passing through the coal. Observations were made on the temperature rise of thermometer F_1. When the maximum temperature was indicated, the air supply was interrupted. The temperature indicated by F_1 gradually fell, due to loss of heat by radiation of the heated zone around the bulb. After a fall of 10° C. the air supply was renewed at the original rate and any rise in temperature on thermometers F_2 and F_3 observed. Any indication of successive maxima on these thermometers would indicate the continued passage of the wave of oxidation along the coal originating from a zone initially heated to the temperature indicated by the first thermometer F_1. These experiments were repeated with reductions in the initiating temperature on the first thermometer F_1 of 10° until the lowest temperature at which the oxidation would proceed was determined.

The experiments were conducted on samples of Arley and Mountain Mine coals, two highly caking coals. The experimental results obtained need not be described fully, but it was found that at the lower limiting temperature the oxidation is very susceptible to small changes in experimental conditions, such as lightness of packing of the coal in the container, and many failures were recorded and many results that appeared to indicate propagation at a very low temperature. Examination of the residue in these last examples indicated an irregular path of oxidation. Taking into account only those experiments in which the oxidation occupied the width of the tube and passed regularly through, 130° C. was indicated with both the coals as the lowest temperature at which oxidation can proceed through the coal under the conditions under which these experiments were carried out. It is interesting that this figure lends support to the contention of Wheeler[3] that, in his series of determinations on the relative ignition temperatures of coals by observing the temperature rise of coal heated in a sand bath compared with the temperature rise in the same bath, the point of self-heating should be taken as that at which the two curves cease to be parallel. A temperature of 125° C. is quoted, which compares closely with the temperature of 130° C. noted above.

It is not desirable to include within the limits of this paper a description of the experiments recently performed on the product remaining after a zone of combustion has traversed a heap of coal. This investiga-

[3] *Trans.* Chem. Soc. (1918) **113**, 951.

tion has been in progress for some years and is approaching the stage when it may be possible to publish definite results. Difficulties have been encountered in attacking the problem because the composition of the residue varies with its position in the heap undergoing oxidation; material near the air supply differs in composition from the portions in the center of the heap. S. H. Jenkins, in association with the author, has made determinations of the decrease in weight that occurs when coal piled into conical heaps undergoes selective combustion. The residual product collected from a number of heaps was found to have undergone similar losses in weight. Fifty experiments were made and the following is offered as an example of the results obtained. The coal used in the experiments was of the bituminous caking variety.

Chemical Analysis of Coal	Per Cent.	Ultimate Analysis on Moisture- and Ash-free Basis	Per Cent.
Moisture	2.5	Carbon	82.21
Ash	7.8	Hydrogen	4.53
Volatile matter	34.1	Nitrogen	1.65
Volatile matter less moisture	31.6	Sulfur	2.10
Coke	65.9	Oxygen	9.51
Fixed carbon	58.1		

Cones of coal weighing about 4 gm. were taken and a zone of combustion made to permeate the mass in a restricted supply of air. The time required for the combustion of the cones was from 1 to 2½ hr. The loss in weight was determined and in five experiments in one group the value was between 4.3 and 9.5 per cent.

The analysis of the oxidation product revealed the fact that it contained 18.2 per cent. of oxygen, whereas the original coal contained 9.5 per cent. The volatile matter evolved from the oxidation product was 28.3 per cent.

Summary and Conclusions

1. Coal has been found to propagate a zone of combustion provided the particles are smaller than a critical size.

2. The rate of propagation of the zone and the temperatures attained depend on the type of coal, the size of the particles of coal, and the availability of the oxygen required for combustion. Temperatures as low as 130° C. during continued propagation of the zone have been recorded.

3. Inert materials, such as rock dust and calcium carbonate, when mixed with coal dust do not inhibit the combustion unless the amount present exceeds 50 per cent. for shale dust and 70 per cent. for calcium carbonate.

4. The oxidation product formed by allowing a zone of combustion to permeate powdered coal in a limited supply of air contains a relatively high percentage of oxygen compared with that present in the original coal.

5. It would appear that if a particular coal can be ground to form a powder, the particles of which are smaller than a limiting size, spontaneous combustion may take place; conditions in the mine that bring about the grinding of coal are consequently contributory factors toward gob fires.

6. Pyrite appears of secondary importance. Thus seams may contain an extremely active form of pyrite and spontaneous combustion be quite unknown; other seams in which the type of pyrite is inactive are liable to fire in the goaf.

7. The investigation emphasizes the importance of making a study of the physical characteristics of coal seams and of the Stopes' ingredients —fusain, durain, clarain, and vitrain.

DISCUSSION

J. D. Davis, Pittsburgh, Pa.—I question whether that combustion is selective or not. Several years ago, when working with oil and anthracite, I noticed that combustion would start pretty much in the same way as was developed by this paper. I do not know just what the limits would be, but after heating and driving out the oil, we got the same sort of propagation of heat through the residue. It is well known that when such a mass is once heated, even at low temperature heat is likely to propagate through the mass.

A. C. Fieldner, Pittsburgh, Pa.—I think the term "selective combustion" used by the author follows the idea expressed some years ago by Professor Wheeler that in the spontaneous oxidation of coal oxygen combines with certain constituents of coal to form carbon-oxygen complexes and that at a higher temperature these complexes break down with the evolution of CO_2 and CO.

The paper presents a novel method of experimentation. It is very interesting that inert materials, such as rock dust and calcium carbonate, when mixed with coal dust do not inhibit the combustion unless the amount present exceeds 50 per cent. for shale dust and 70 per cent. for calcium carbonate. These figures are of the same order as the amount of inert dust required to prevent propagation of coal dust explosions in a suspension of dust in air. Shale and limestone dust are about equally effective in stopping propagation of dust explosions.

I am not entirely clear as to the experimental evidence in the paper justifying the seventh conclusion—namely, mention of studying the Stope's ingredients, fusain, durain, clarain, and vitrain. It may be very important to determine the selective combustion of these constituents but the author does not include any experiments with these ingredients in his paper except in the case of fusain.

Is it not possible to explain most of the combustion phenomena described in the paper by simple surface combustion of the fine particles of coal? The combustion proceeds from one end of the loose pile to the other, using up the available oxygen in the interstices between the coal particles. It does not seem necessary to presuppose that it is selective combustion of certain constituents. It may be uniform combustion of the coal particles in contact with the air film. If the pile is allowed to cool and air diffuses into it again, the phenomenon can be repeated. It seems likely that instead of selective combustion the phenomen is simply one of combustion of the coal in contact with oxygen films on the surface of the particles.

George S. Rice,* Washington, D. C.—The mother of coal, fusain, seems to be the one constituent with which they have the most trouble in spontaneous fire in the mines. In Central Illinois, practically every mine has fires, especially during warm weather. We do not know the cause. There have been some attempts to determine that but, as the coal has a high sulfur content, pyrite has been one of the suspected causes. This paper seems to discredit pyrite but I have never lost the belief that pyrite is a factor in this combustion. Various iron mines of Michigan have spontaneous fires and very fine particles of shale thrown on a dump take fire.

W. M. Grant, Birmingham, Ala.—The most striking omission in the paper is that there is no statement as to what change in the chemical composition of this coal resulted from this combustion; it seems to me that would be a factor.

J. D. Davis.—Possibly fusain is more susceptible to heating by this method because it absorbs oxygen more readily than the other constituents. I do not know that that has been tried out, but I would think that would be the case.

George S. Rice.—Has any work of exactly this kind been done? I am not familiar with the details, but to me this was an entirely new idea as to the actual demonstration of combustion.

H. J. Rose, Pittsburgh, Pa.—So far as I know, no detailed study has been made before. However, the slow progressive combustion of coal is not an unfamiliar phenomenon, and is sometimes noted in the course of handling pulverized laboratory samples. A short time ago we found that a particular sample of coal screenings, most of which would pass a 1/16-in. screen, would catch fire overnight in a steam-heated drying oven. So far as we know, the temperature never exceeded 110° C. I

* Chief Mining Engineer, Bureau of Mines.

do not know the percentage of fusain in this coal, but there may have been considerable.

S. W. Parr, Urbana, Ill.—The paper coincides with some work we are doing. All material, and coal material especially, has a tremendous avidity for oxygen, and the finer it is divided the more oxygen it takes up. Those coals that have the most hygroscopic water in their texture still further accentuate the possibility of taking on oxygen by the fact that that water goes out, and something must come in. It is a selective absorption process for oxygen in preference to nitrogen or carbon dioxide. Evidence is beginning to accumulate, and there is a lot of it, that this oxygen is a surface condensation, which is a highly concentrated form of oxygen, is a film over all the surface, including the internal structure of material that is porous. As a result, coal that is already in a fine state of division, such as mother of coal, has the start on the particles that are still in the massive form.

We need to study the behavior of this oxygen in these low-temperature ranges, because this oxygen, given time enough, will gradually go over into a chemical combination with certain compounds of the coal, which readily split off, H_2O, and a little later CO_2. Normally, in the course of time, you can speed this up in certain ways. The whole problem of spontaneous combustion is to know how to speed it up.

The author touches a Bunsen burner to the coal. If by means of a match, a spark, or friction or anything you start the heat, combustion will go through the pile, and the combination of that condensed oxygen will be the only thing that takes place. If you let the pile stand long enough to take on more oxygen, the heat will go through again, but only to the extent of the oxygen absorbed in the mass. If fusain absorbed oxygen, is it not as good a kindling medium as vitrain, xylan or lignose compounds? But the point is, how to get the combustion started. We have a lot of data confirming Wheeler's data that the point of ignition is about 150° C.; that is an ignition point. From that point on it will burn autogenously, but only to the extent it is permeated by oxygen.

In the case of pyrites, combustion will not start of itself, but if there is a lot of finely divided pyrites, and plenty of oxygen has been absorbed and the combustion is started, it will continue. What we want to find out is what starts the heat. Pyrites, if heated above 100° C. and furnished with the oxygen and moisture, will fire autogenously and make heat enough to burn more pyrites and carbon. On the other hand, carbon oxidation will generate the heat and start combustion of the pyrites.

David White, Washington, D. C.—The nature of the paleontological agglomerates composing the coal justifies the assumption that coal of a rank so high even as high bituminous is still an agglomerate chemically.

Accordingly, I do not see why such oxidation is not selective both at the initial point and later.

Some of the experimental observations made of thin sections of coal, as the temperature is raised, seem to indicate different (selective) responses in the component matter when, by accident or otherwise, oxygen finds its way into the furnace.

Nitrogenous Constituents of Coal

By John W. Cobb,* Leeds, England

(New York Meeting, February, 1925)

The attempts of British investigators to arrive at definite knowledge concerning the nature of the nitrogenous constituents of coal have been mainly made through studies of the behavior of coal on carbonization and gasification. There have been carried out numerous determinations of the distribution of nitrogen in the products of carbonization under laboratory and large-scale conditions; and by a careful consideration of the extent to which nitrogen is liberated, say as ammonia, at different temperatures and under different conditions of operation as regards atmosphere, it has been possible to form some general notions as to the nature of the nitrogenous compounds present in the coal, and at the same time to arrive at clearer ideas as to what are the important operative factors in determining the ammonia yield under working conditions. This work has been spread over many years and is summarized below. The difficulties of connecting the results in such a way as to allow of the nitrogenous constituents of the coal being described in terms of specific organic structure are great. They arise, for example, in the carbonization process, because the phenomena of decomposition observed at any one temperature can only refer to compounds decomposing at that temperature, each of them with a previous history of chemical transformations occurring at lower temperatures. To put it in another way, the compounds occurring in the coke at any stage are not in the least likely to be those present in the original coal. The same difficulty, in a milder form, occurs when the method of differential solution is attempted. There is always the preliminary question, almost impossible to answer, as to how far the separation by the use of the solvent has involved some form of decomposition of the original compounds. In the following summary, an attempt has been made to bring together results obtained by British workers.

*Livesey Professor of Fuel and Gas Industries, Leeds University.

Foster,[1] Watson Smith,[2] Wright,[3] Anderson and Roberts,[4] Short,[5] McLeod,[6] Illingworth,[7] and Foxwell[8] have shown that on heating coal the nitrogen is first liberated in the form of ammonia between the temperatures of 310° and 400° C., and the evolution continues with rising temperature. The large-scale carbonization of coal yields an average distribution of the total nitrogen of the coal as follows:

Nitrogen as ammonia	10–20 per cent.
Nitrogen left in the coke	40–80 per cent.

The remainder is found as free nitrogen, cyanogen (and a little of the pyridine bases) in the gas and in the tar. Tervet,[9] with confirmatory experiments by Beilby[10] and Anderson and Roberts, showed that the passage of hydrogen over coke at a red heat liberated, as ammonia, a portion of the nitrogen left in the coke. Christie,[11] on the other hand, using hard metallurgical coke, showed that no reduction of the nitrogen compounds in that coke occurred by the use of a stream of hydrogen.

Monkhouse and Cobb[12] made detailed experiments on cokes manufactured from the same coal at different temperatures. They investigated the influence on the nitrogen compounds of: (*a*) The temperature of coking; (*b*) heating in an inert current of nitrogen; (*c*) heating in a current of hydrogen; and (*d*) heating in a current of steam. They found that, with a low-temperature coke (500° C.) heated to 800° C., part of the nitrogen of the coke was liberated as ammonia in an inert current of nitrogen, with a further liberation of nitrogen, as ammonia, in a current of hydrogen, and the remainder was liberated as ammonia on gasification of the coke with steam. With a hard (1100° C.) coke, however, the nitrogen was only liberated as ammonia by the gasification of the coke with steam. They concluded that there occurred in the coal nitrogen compounds that on distillation yielded: (1) Ammonia directly on heating; (2) compounds that, in the presence of hydrogen, decompose forming ammonia; (3) resistant compounds, the so-called carbon nitrides,

[1] William Foster: *Jnl.* Chem. Soc. (1883) **43**, 105.

[2] Watson Smith: *Jnl.* Chem. Soc. (1884) **45**, 144.

[3] Lewis T. Wright: *Jnl.* Chem. Soc. (1884) **45**, 99.

[4] W. Carrick Anderson and James Roberts: *Jnl.* Soc. Chem. Ind. (1898) **17**, 1013; (1899) **18**, 1099.

[5] Andrew Short: *Jnl.* Soc. Chem. Ind. (1907) **26**, 581.

[6] James McLeod: *Jnl.* Soc. Chem. Ind. (1907) **26**, 137.

[7] S. Roy Illingworth: *Jnl.* Soc. Chem. Ind. (1920) **39**, 111T.

[8] Foxwell: *Fuel in Sci. & Prac.* (1924) **3**, 227.

[9] Robert Tervet: *Jnl.* Soc. Chem. Ind. (1883) **2**, 445.

[10] George Beilby: *Jnl.* Soc. Chem. Ind. (1884) **3**, 216.

[11] Christie: Dissertation, Aachen, 1908.

[12] Monkhouse and Cobb: *Trans.* Inst. Gas Eng. (1920–21) 543; (1921–22) 137.

which are uninfluenced by hydrogen but which can be decomposed by the use of steam with the liberation of ammonia.

It appears that as the temperature of the coal is raised the nitrogen remaining in the coke passes into a combination more resistant to the action of heat and to the influence of hydrogen, until in the hard metallurgical coke the only method of liberating the nitrogen is by the use of steam with a consequent breaking up of the carbon and nitrogen containing molecule.

How far the original coal contains nitrogen in these different forms and how far they are formed subsequently on heating are at present unknown, but preliminary experiments by Monkhouse and Cobb on the distillation of glycocoll showed that with such a compound, containing a single amino group, the whole of the nitrogen was not obtained as ammonia but a portion remained in the residue.

From the work of Wheeler,[13] Bone,[14] and others, on the action of solvents on coal, nitrogen appears to be an intrinsic part of most of the compounds in coal; no preferential separation of the nitrogen compounds is obtained.

There are other secondary decompositions of the nitrogen compounds of coal that occur to a small extent, causing the formation of cyanogen in the gas and of nitrogen in the tar.

The nitrogen compounds existing in high-temperature coke have been further investigated by Pexton and Cobb.[15] The rate of gasification of the carbon and nitrogen of the coke, using steam, was examined; they found that the ratio of the two elements remained constant during gasification. With a low-temperature coke (800° C.), the constant ratio did not hold during the early stages of gasification but obtained during the later stages.

The behavior of coal on carbonization under different conditions would be consistent with the view that the characteristic mode of occurrence of nitrogen in coke is as a carbon ring structure with nitrogen existing in the nucleus. It is interesting to note that Pearson,[16] in his work on the ulmins of coal, states that the nitrogen is held with great stability in oxidized ulmins and that this resistant nucleus is probably cyclical.

Attention may be drawn to the industrial importance of the work done in England by the late Ludwig Mond and others in the development of the "Mond gas" process, in which was demonstrated the practical possibility of obtaining from coal, at the same time, a good producer gas and a high yield of ammonia corresponding with some 60 to 70 per cent.

[13] Arthur Herbert Clark and Richard Vernon Wheeler: *Trans.* Chem. Soc. (1913) **103**, 1704.

[14] Bone: *Proc.* Roy. Soc. (1919) **96**, 119; (1922) **100**, 582; (1924) **105**, 608.

[15] Pexton and Cobb: *Trans.* Inst. Gas Eng. (1922–23); *Gas Jnl.* (1923) **163**, 160.

[16] Pearson: *Fuel in Sci. & Prac.* (1924) **3**, 297.

of the total nitrogen present in the coal. The elaboration of the plant needed and the high steam consumption, and the production of synthetic ammonia in large quantities, render the Mond process commercially less attractive than it was ten years ago, but various attempts are being made to introduce in it those modifications that present conditions require.

DISCUSSION

S. W. Parr, Urbana, Ill.—What is meant by the sentence "coal, upon carbonization, will be characterized by the occurrence of nitrogen in coke; there is a carbon-ring structure which retains its ring form in coke"? In the earlier part, the paper referred to those stable nitrogen compounds, which are nitrogen carbon, a compound in the coke which is quite distinct from the ring compound.

H. J. Rose, Pittsburgh, Pa.—He mentions them as "nitrides" in quotation marks. V. B. Lewes appears to have believed that complex nitrogen compounds occurred in coke. Nitrogen compounds have been reported in pitch coke.

S. W. Parr.—Yes, but pitch is not coke.

Reinhardt Thiessen, Pittsburgh, Pa.—One of the points I have tried to bring out in this and preceding papers is that a large number of plant compounds contain the nitrogen atom as a part of the ring in the molecule. Every plant chemist knows that all plants contain alkaloids. While there may not be a large percentage of the alkaloids in one plant, the production of the alkaloids as a whole is large. The plant secretes alkaloids and disposes of them as secretions and stores them in certain tissues.

S. W. Parr.—Suppose we take sugar carbon; there is no ring structure or anything else, it is simply carbon. If we mix with that some nitrogenous compound, not free nitrogen, we will have a limited amount of nitrogen, up to 3 or 3½ per cent. Has that nitrogen jumped into some ring form and made a combination with the carbon or that coke? We do not have to have a ring compound to get nitrogen into the coke at all.

Reinhardt Thiessen.—Could you add the nitrogen in the form of albumin?

S. W. Parr.—Any kind of nitrogenous compound.

Reinhardt Thiessen.—In albumin, the nitrogen is in a ring of the molecule and albumin cokes; you have a residue there.

S. W. Parr.—Very true; but I cannot think of it as staying in an organic ring compound over into the coke form.

Reinhardt Thiessen.—Not if you add free nitrogen or ammonia?

S. W. Parr.—I cannot recall results on ammonia.

Reinhardt Thiessen.—Of course, I do not want to infer that all nitrogenous compounds in coal are in the form of ring compounds; a very large number of nitrogenous compounds are not ring compounds. Bacteria and fungi hydrolyze many plant substances and use for their energy supply those products that are fermentable. In the case of the glucosides, part of the hydrolytic products contain, besides the glucose, a ring compound. The former is fermentable, but the latter is not and contributes to the bog.

The alkaloids are ring compounds in which a nitrogen atom forms part of the ring. These compounds are ordinarily not fermentable. The following are a few well-known members of the alkaloids: piperidine, nicotine, conine, quinoline, quinine, strychnine, cinchonine, cocaine, and atropine. The purine bases form another group of plant compounds in which nitrogen atoms form part of the ring. All of these ring compounds are relatively stable and not attacked ordinarily by micro-organisms.

Coal and Oxygen

By S. W. Parr* and F. B. Hobart, Urbana, Ill.

(New York Meeting, February, 1925)

Studies relating to the behavior of coal toward oxygen may have for their purpose the determination of the fundamental factors that underlie spontaneous combustion, weathering and deterioration, and the general topic of storage, as well as those properties that have to do with the underlying principles of carbonization. There is also involved the possibility of developing information relating to the constitution of coal, or at least the chemical properties inherent in the type substances of which the coal is composed. It is the purpose here to record certain

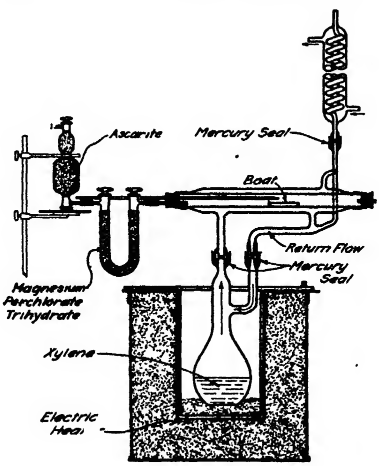

Fig. 1.

results bearing on this latter idea of the chemical properties that characterize the main constituents of bituminous coal.

The avidity of freshly mined coal for oxygen has long been known. What happens to the coal or to the oxygen is not so clear. Is the oxygen absorbed or chemically combined, and what are the conditions as to time, temperature, texture, or components that are most involved in the phenomenon?

If we subject a weighed quantity of coal maintained at a constant temperature to a current of oxygen, we may obtain three factors of interest—the weight increase of the coal, the weight of the water, and the weight of the carbon dioxide formed in the reactions involved at that

* Professor of Applied Chemistry, University of Illinois.

temperature. In the apparatus shown (Fig. 1) 20 gm. of coal, ground to pass through a 60-mesh sieve, is subjected to a high vacuum until moisture-free before being subjected to the oxygen atmosphere. The

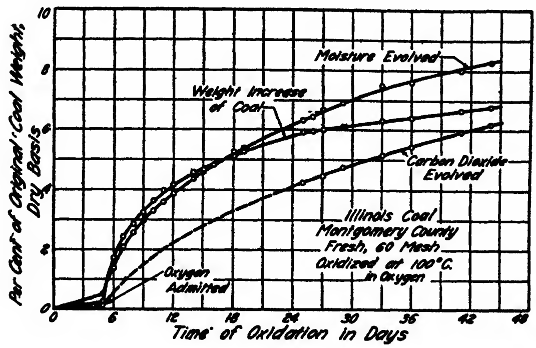

FIG. 2.

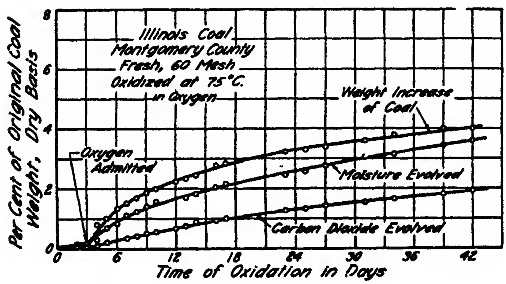

FIG. 3.

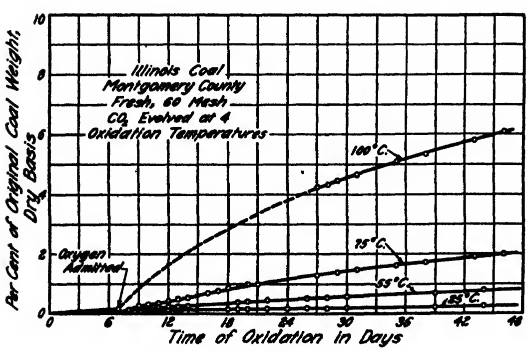

FIG. 4.

specific temperature is maintained by using in the flask a liquid having the desired boiling temperature, using xylene for 140°, water for 100°, carbon tetrachloride for 75°, etc. At first weighings are made daily;

later, as the reactions become less pronounced, at two or three day periods. For weighing, the boat is transferred to a tube with telescoping cover for protecting against moisture changes while cooling and weighing. Fig. 2 shows the log of weights covering a period of 44 days; the striking fact is the constant increase in weight, notwithstanding the continuous

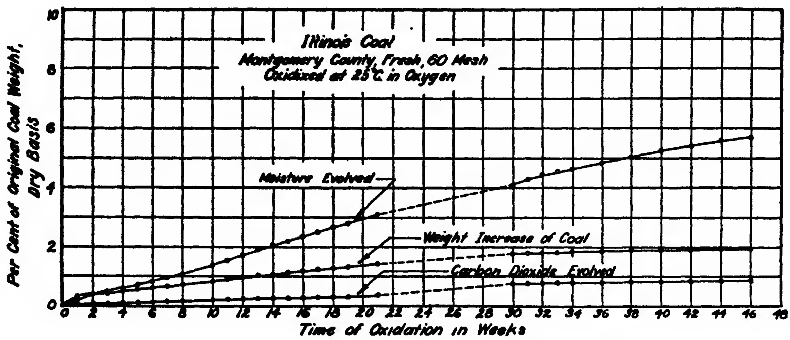

FIG. 5.

discharge of H_2O and CO_2. A notation should be made concerning the preliminary period of five days in which the attempt is made to bring the system to an equilibrium by passing dry purified nitrogen through the apparatus. In the chart, as shown, there is a small evolution of water at 100°, accompanied by a slight increase in weight; the latter is

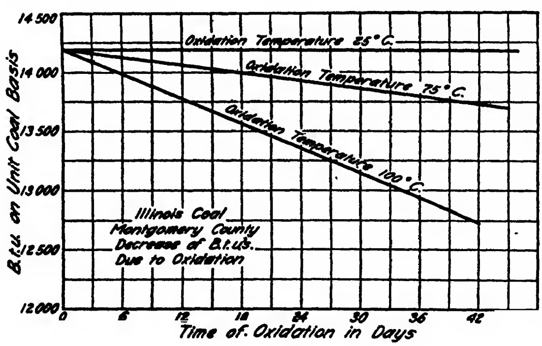

FIG. 6.

probably due to nitrogen absorption, the former to activities already possible in the coal substance. They are not of sufficient moment to affect the main reactions that are in evidence on the admission of oxygen, as shown following the fifth day.

The corresponding values for temperatures other than the one shown are similar but vary in amount for a given period, as shown in Fig. 3.

This fact is also shown in Fig. 4, where the values for CO_2 as derived at different temperatures are assembled for illustrating this point of accelerated activity at higher temperatures. At room temperatures, the reactions are so slow as to require graduations to be shown in weeks instead of days; Fig. 5 gives the values for tests running through a period of 46 weeks. In comparing these values with those of Figs. 2 and 3, it is to be remembered that the amount of increase per week, if extended to correspond to the daily changes of the higher temperatures, would

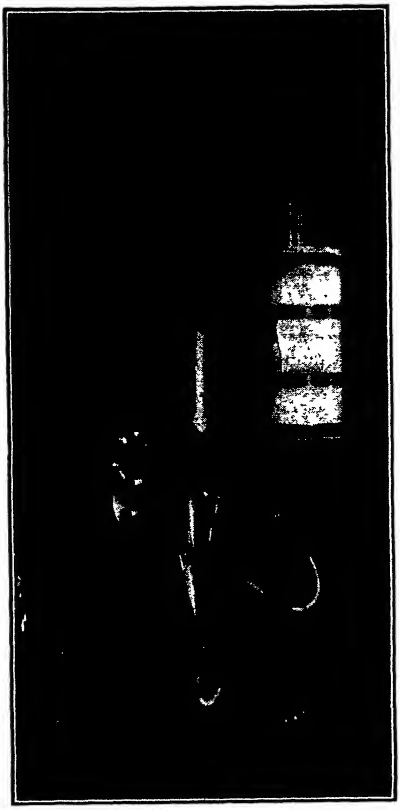

Fig. 7.

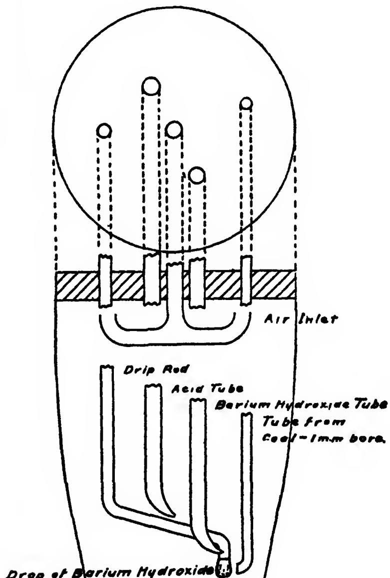

Fig. 8—Carbon-dioxide detection tube.

show the relationship to be the same as to the type of reaction, but varying only in degree. A notation may be made to the indication suggested, especially in Fig. 5, that the accession of oxygen is first as an adsorbed constituent, from which it enters into molecular combination by addition. By heat, or after long time, the reactions proceed to the point of breaking down to the extent of discharging H_2O and CO_2. In much the same way, the reactions with air instead of oxygen are of the same order but less in amount for a given period of time.

If we have a parallel apparatus running under precisely the same conditions on the same coal, from time to time we may take out gram samples in their respective capsules for determining at various stages

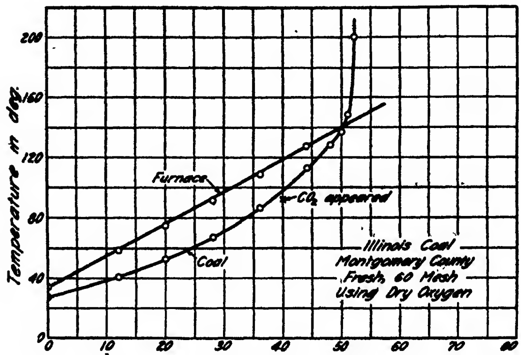

FIG. 9.

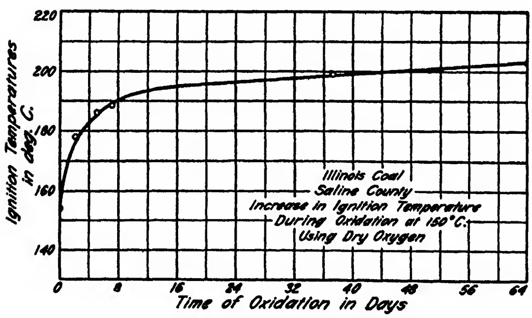

FIG. 10.

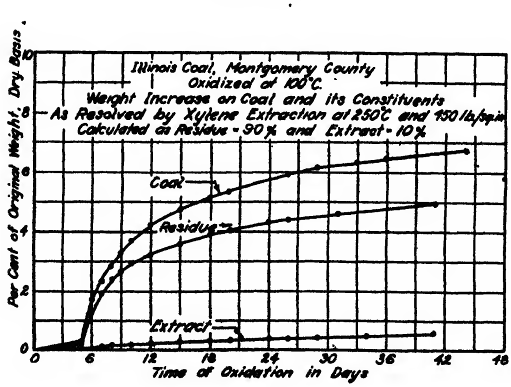

FIG. 11.

the calorific values. The main samples in the boat containers, as represented in Fig. 1, also furnish samples for this purpose at the end of the

experiment. A charting of the B. t. u. values derived from these conditions is made in Fig. 6; the almost complete absence of oxidation losses at 25° are consistent with the discharge of CO_2 for that temperature, as shown in Fig. 4. A similar agreement for the other temperatures is shown between the loss in heat values, Fig. 6, and the weight of CO_2 discharged, as shown in Fig. 4.

Another series of tests was made on the same coals to determine the ignition temperatures in a current of oxygen, the apparatus being arranged to give also an indication for the appearance of CO_2 when that product began to be discharged in sufficient volume to indicate positive chemical combination with oxygen. The method is similar to the one used by Parr and Francis[1] and Professor Wheeler;[2] the apparatus as designed by C. C. Coons[3] is shown in Figs. 7 and 8. These values for a type coal are shown in Fig. 9. In order to show the average values for coals of the Mid-Continental type, the ignition temperatures for a number of such coals are given in Table 1.

TABLE 1.—*Ignition Temperatures of Illinois Coals*

	Ignition Temperature, Degrees C.
Perry Co., Majestic Mine, DuQuoin	158
Perry Co., Dowell Mine, DuQuoin	159
Perry Co., Willisville Mine No. 6	157
Perry Co., Clinch	157
Perry Co., Gayle Coal Co., Strip Pit	153
Perry Co., Scott Smith Co., Strip Pit	152
Jackson Co., Consol. Coal Co. No. 9	159
Jackson Co., Gus Blair Mine No. 3	159
Jackson Co., Carbondale	169
Jackson Co., Murphysboro No. 1	167
Jackson Co., Murphysboro No. 2	153
Jackson Co., Murphysboro No. 3	157
Vermilion Co., Westville	153
Vermilion Co., Danville Strip Mine	153
Randolph Co., Percy	159
Williamson Co., Herrin	159
Franklin Co	153
Marion Co., Odin	159
Saline Co., Harrisburg	157
Montgomery Co., Nokomis	153
Sangamon Co., Riverton	153
Grundy Co., Leland Mine No. 7, Verona	152
Madison County, Livingston	147

Suppose that we maintain corresponding samples of coal in a current of air at 150° C. for specific periods of time and plot the ignition tempera-

[1] S. W. Parr and C. K. Francis, Univ. Ill. Eng. Exp. Sta., *Bull.* 24 (1908).
[2] *Jnl.* Chem. Soc. (1918) **113**, 945.
[3] S. W. Parr and C. C. Coons, *Ind. & Eng. Chem.* (1925) **17**, 118.

tures as the oxidation absorption increases; these results, shown in Fig. 10, indicate a positive change in the coal substance.

We come now to some data obtained from the combination of oxygen with that constituent of coal, for want of a better term, designated as the cellulosic residue. It is apart from our purpose to attempt to account for or even classify this constituent further than to say that it is the

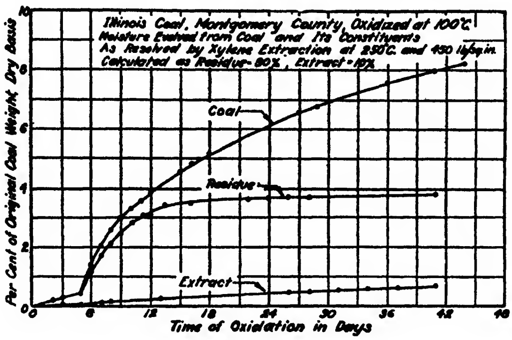

FIG. 12.

insoluble residue left after prolonged extraction of the soluble components of an Illinois coal with xylene. This residue, after thorough washing, was maintained in contact with oxygen at a temperature of 100° C. until the substance had become saturated to the limit of its absorptive capacity with oxygen. The soluble extract was oxidized in a similar manner. In Figs. 11, 12, and 13, the weight increase, water, and CO_2

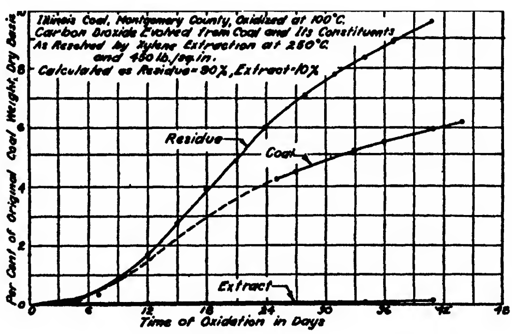

FIG. 13.

evolved for the original coal, insoluble residue, and soluble extract are given. These values show distinctly the pronounced activity of the insoluble or cellulosic residue.

By submitting oxidized insoluble residue to the process of fractional decomposition and comparing the results obtained at the same temperature on a fresh unoxidized sample, the values given in Tables 2 and 3 are obtained. The most significant temperature over the range used

was at 300° C. and the analysis of the gas yield at that temperature is given for fresh and oxidized coal in its normal state and for the residue insoluble in xylene from the same coal similarly treated in the fresh and oxidized condition. The avidity of this part of the coal constituent for oxygen is certainly marked and serves to define the character of this material as being of the humic or residual cellulosic rather than of the resinic type. Going back also through the experiments, as outlined, indicating the oxygen absorption and discharge as H_2O and CO_2, it is at once apparent as to the coal component involved in the reactions, as also its general character and the part it plays under such conditions as storage, weathering and carbonization.

TABLE 2.—*Constituents at* 300° *C. in Cubic Centimeters per* 100 *Gm. of Coal*

	Fresh	Oxidized
CO_2	85.5	1073.1
Illuminants	4.0	11.5
O_2	4.8	4.5
CO	21.2	196.2
H_2	3.7	.7
CH_4	19.8	29.3
C_2H_6	9.6	24.4
Total volume	148.6	1339.7

TABLE 3.—*Constituents at* 300° *C. in Cubic Centimeters per* 100 *Gm. of Coal Residue Insoluble in Xylene*

	Fresh	Oxidized
CO_2	153.2	1423.0
Illuminants	5.2	2.4
O_2	7.6	2.7
CO	48.5	191.2
H_2	10.5	3.1
CH_4	13.2	2.4
C_2H_6	5.1	0.0
Total volume	243.3	1624.8

DISCUSSION

J. D. DAVIS, Pittsburgh, Pa.—I agree that we have got to find out what starts the combustion. We have to go to find out the sensitivity of the coal to those low temperatures. The author is working on the lines of the rate of absorption of oxygen; at the Bureau of Mines, we are studying the rate of heating. We have found that the two methods agree so far as we have been able to check them and that the rate of spontaneous heating is proportional to the rate of absorption of oxygen. I was going to ask if the author has studied the effect of mixing coal that had been oxidized with fresh coal. Men having storage problems believe that fresh coal should not be placed on top of old coal, that a fire will result if it is.

This experiment of determining the amount of carbon dioxide by distillation shows conclusively why a coal that has been oxidized or weathered would not work well in a combustion furnace. It explains very well the fact that the CO_2 would form a sort of a blanket over the fire and restrict combustion. Did the author find that the humus matter, or the residue that he obtained by extracting the coal, absorbed other gases more readily than charcoal? It might be a question of physical absorption there rather than chemical.

W. T. THOM, JR.,* Washington, D. C.—When looking over analyses of samples from the Rock Springs field, Wyoming, I recall noting that samples of supposedly fresh coal collected from new crosscuts, 20 ft. from 38-year old workings, actually showed a large loss of B.t.u. value, and an increase in oxygen content and in apparent moisture content. I assume that the process of alteration in that instance is similar to that producing the change shown by the authors' 25° curve, except for the greater change due to the great lapse of time in the case of the Wyoming samples.

S. W. PARR.—I have a chart in which these measurements have been taken at 25° and at normal temperature for seven months; they are precisely the same, only the angle is lower. As a verification of that if we prepared a sample under the standard conditions for the analysis of a fresh coal, ground it in a jar mill, and enclosed it in a stoppered bottle (the sample was not oven dried, but dried at ordinary temperature of equilibrium), if we have occasion to repeat the work we would not think of taking the moisture value that we found on the coal originally. Invariably, it will have a higher moisture factor, perhaps only ½ per cent. or so.

At an outcropping of coal in Peoria County, samples of coal were taken and analyzed; they gave identical factors for a lignite, up to 20 per cent. of moisture and heat value, referred to the unit coal bases, for a lignite; that is below 14,000 B.t.u. per lb. of unit material. That was rather striking. We had not been willing to concede at any time that Illinois had any lignite coal, but when this working got back 100 ft. the coal was normal, absolutely like other coal in that zone.

In our investigations, we have not tried any coal mixtures, but there is a good deal in the suggestion that this stage of catalytic activity may put old weathered coal in a mood to operate more readily on a fresh coal if they are mixed.

H. J. ROSE, Pittsburgh, Pa.—Regarding the gases given off by the residue from oxidized coal, does that mean the residue from the extract?

S. W. PARR.—Yes.

* Geologist in Charge of Geology of Fuels, U. S. Geological Survey.

H. J. Rose.—We know that coal-seam outcrops are highly modified, but I presume they have not been exposed to temperature greatly in excess of 25° or 30°.

S. W. Parr.—I do not know whether it would be consistent to answer that question by saying that at normal temperature, if the time is long enough, you will have this degradation of heat value and all these others.

H. J. Rose.—A matter of centuries, for instance?

S. W. Parr.—A matter of centuries, or at least, a good many years. Coal that started out in the lump form, that has been in storage for six years, does not show, let us say, over 2 or 3 per cent. of loss of heat. We ought not to generalize from so few illustrations, but the loss of this value at normal temperature is exceedingly low for any common length of time. But when you increase the time several years, it results in great loss of heat value. There may be exceptions to that, but as far as our coal is concerned, it seems to be substantiated.

A. C. Fieldner, Pittsburgh, Pa.—Is the absorption of oxygen essentially one of absorbing oxygen in the unsaturated bonds of the chemical compounds in coal which later on at higher temperature split off water, CO_2, or CO?

S. W. Parr.—In general I would say yes; but there is much about that matter that is obscure and hard to put your finger on. My explanation would be that it first goes over into unsaturated compounds of the ring type; and then as that action becomes completed, even at normal temperature, it begins to split off. But if you increase the temperature when that split off comes, a little heat is generated. Everything that we are doing would seem to give a basis for the idea that first there is adsorption, then oxygen enters into the compound, and, in the course of time, there is the splitting off into H_2O and CO_2.

F. F. Jorgensen, Gillespie, Ill.—Were any experiments made in the storing of coal by shutting off the oxygen?

S. W. Parr.—Yes; we can store screenings just as well as anything else indefinitely, provided we shut off the oxygen. You cannot leave any possible holes such as would come from posts or girders or large lumps, to let the air in; but if you pack in fine coal, it will keep just as well as any kind. Thousands of tons are being stored that way now.

F. F. Jorgensen.—You do not shut off all the oxygen; a limited supply of oxygen will stop that rise in heat and eventually the combustion of the coal.

David White, Washington, D. C.—The lignite keeps as well as fine Illinois coal, for example, if moderately compressed.

S. W. Parr.—I would hesitate to take any chances with lignite, but theoretically, you could store a lignite, sealing it so that no air could penetrate; but what is going to happen when you dig out some of that lignite and ship it a short distance, and the water it loses is replaced by oxygen?

W. M. Grant, Birmingham, Ala.—The Northern Pacific Railroad is burning some lignite in its locomotives for the first time. It only allows about three weeks between the mining and consumption, because it has no place for storing the fuel any longer than that.

David White.—Possible economies, if not more important results, would be effected by taking coal immediately from the mines and putting it to the retort process before it had a chance to take any oxygen. In all of our experiments on coal, we must take the greatest precautions to get materials as fresh as possible. The conventional analysis apparently represents more or less oxidized fuel in every sample except those of the highest ranks.

Modern Views of the Chemistry of Coals of Different Ranks as Conglomerates*

BY A. C. FIELDNER,† AND J. D. DAVIS,‡ PITTSBURGH, PA.

(New York Meeting, February, 1925)

THE older coal chemist had a much simpler conception of coal than we have today. To him coal was a mineral composed essentially of carbon, hydrogen, oxygen, nitrogen, sulfur, ash, and water, in various proportions. His studies on the constitution of coal were directed along the conventional lines of proximate and ultimate chemical analyses and making deductions from these data without any real appreciation of the fact that coal is a conglomerate of various chemical compounds, including many of the most complex structures known to organic chemistry.

The view of the modern coal chemist is well expressed by Franz Fischer,[1] who says that while proximate and ultimate analyses are important both from the scientific and technical point of view, they tell the chemist no more concerning the number and kinds of chemical compounds that constitute coal than the reader would learn of the contents of a book if told that the printed contents consisted of 15 per cent. of the letter "e," 5 per cent. of the letter "n," 1 per cent. of the letter "g," 4 per cent. of the letter "b," etc. As the reader must have the grouping of letters into words and words into sentences, so the chemist must have the grouping of atoms into molecules and the proportion of each molecular compound in the coal aggregate before he acquires an adequate knowledge of the constitution of coal. Modern investigators[2] are laying the foundation of a new chemistry of coal based on the biochemistry of plants and the chemical changes involved in processes of fermentation and decay. As

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* Published by permission of the Director, Bureau of Mines.

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‡ Fuels chemist, Pittsburgh Experiment Station, Bureau of Mines.

[1] Franz Fischer: Ueber den Stand der Kohlenforschung Schriften der Brennkrafttechnischen Gesellschaft, E. V. Nr. 1, Wilhelm Knapp, Halle (Saale) 1919, p. 5.

[2] David White and Reinhardt Thiessen: Bur. of Mines *Bull.* 38 (1913).

Marie C. Stopes and R. V. Wheeler: Monograph on Constitution of Coal. Dept. of Sci. & Ind. Research, London (1918). Reviewed in *Fuel in Sci. & Prac.*, 1924 issues.

Reinhardt Thiessen: Structure in Paleozoic Bituminous Coal. Bur. of Mines *Bull.* 117 (1920).

Franz Fischer and Hans Schrader: Entstehung und Chemische Struktur der Kohle—Kaiser-Wilhelm Institut für Kohlenforschung in Mülheim-Ruhr. Verlag W. Girardet, Essen, 1922.

coal was formed from plant matter and as plant chemistry is better known than coal chemistry, it is most logical to start with the chemistry of plant constituents and of the known products obtained under the various possible modes of decomposition under peat- and coal-forming conditions. American investigators, in particular White and Thiessen, are attacking the problem by this method. From the point of view of paleobotany and biochemistry, they are endeavoring to trace the original plant constituents through the successive geological stages in coal formation, as exemplified in the coals of different ranks from peat to anthracite.

In England, Wheeler and his co-workers are intensively engaged in separating individual constituents or similar groups of constituents in coal and comparing their properties with similar constituents of the plants of today. In Germany, Franz Fischer and associates at the Coal Research Institute at Mülheim-Ruhr, are vigorously attacking the problems of the constitution of bituminous and brown coals by chemical methods of extraction with solvents, reaction with various reagents, decomposition by heat and pressure, and correlation of these results with a study of the biochemistry of the two principal plant constituents, lignin and cellulose.

These are the leaders of research on the constitution of coal who are laying the foundation for our modern coal chemistry, which we will summarize briefly, using the American method of classifying coal by ranks.

Classification of Coal by Ranks

The U. S. Geological Survey[3] uses the word "rank" to designate those differences in coal that are due to the progressive change from lignite to anthracite, a change marked by the loss of moisture, oxygen, and volatile matter; and by an increase of fixed carbon.

The classification of coal by ranks is essentially geological, and assumes a generally common origin from vegetable deposits analogous to peat. The difference in rank is due to subsequent biochemical and geological action rather than to essential differences in the original vegetation. Within the same rank there may be groups of coals of special characteristics that may be due to differences in the original material, as for example, the cannel and boghead coals in the bituminous rank.

The various ranks assigned to American coals in progressive order, beginning with the youngest stage in coal formation, are lignite, subbituminous, bituminous, semibituminous, semianthracite, anthracite. The bituminous rank is again subdivided into low-, medium-, and high-rank bituminous coal; and the semibituminous into low- and high-rank semibituminous coal.

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[3] M. R. Campbell: The Coal Fields of the United States. U. S. Geol. Surv. *Prof. Paper* 100-A (1917) 3.

The criteria for classification are simple chemical tests and physical characteristics of the coal; the proximate analysis is sufficient to differentiate the ranks from bituminous to anthracite, but physical characteristics are essential in addition to the proximate analysis for identifying subbituminous coals and lignite. The distinguishing chemical and physical characteristics are given in Table 1.

TABLE 1.—*Chemical and Physical Characteristics of Various Ranks of Coal*

Rank	Chemical Characteristics		Physical Characteristics
	Approximate Moisture[a] Content, Per Cent.	Fuel Ratio $\frac{F.C.}{V.M.}$	
Lignite	30 to 45		Distinctly brown; either markedly clay-like or woody in appearance; falls into pieces on exposure to weather.
Subbituminous	18 to 30		Black; no distinct woody texture; disintegrates and loses moisture on exposure to weather but less rapidly than lignite.
Bituminous	3 to 15	3	But slightly affected by exposure to weather.
Semibituminous	3 to 6	3 to 7	But slightly affected by exposure to weather.
Semianthracite	3 to 6	6 to 10	But slightly affected by exposure to weather.
Anthracite	2 to 3	10 to 60	But slightly affected by exposure to weather.

[a] Normal mine moisture.

A graphic representation[4] of the proximate chemical analysis of the various ranks of coal and their calorific values is given in Fig. 1. Diagram (*b*) shows the progressive increase of fixed carbon from lignite to anthracite; diagram (*a*) shows a progressive increase in the calorific value from lignite to low-rank semibituminous coal. A diminution of calorific value then takes place as a result of the decrease in hydrogen content as the rank changes to the anthracites. Similar progressive increases in the total carbon content and decreases in oxygen content are found in passing from lignite to anthracite. It is therefore evident that the oxygen content (or the carbon and hydrogen content as proposed by Seyler[5] in England) can also be used as a chemical criterion of the rank of a coal, as oxygen elimination is a progressive factor in coal formation. From the

[4] M. R. Campbell: *Loc. cit.* 8.

[5] Clarence A. Seyler: *Fuel in Sci. & Prac.* (1924) **3**, 15, 41, 79.

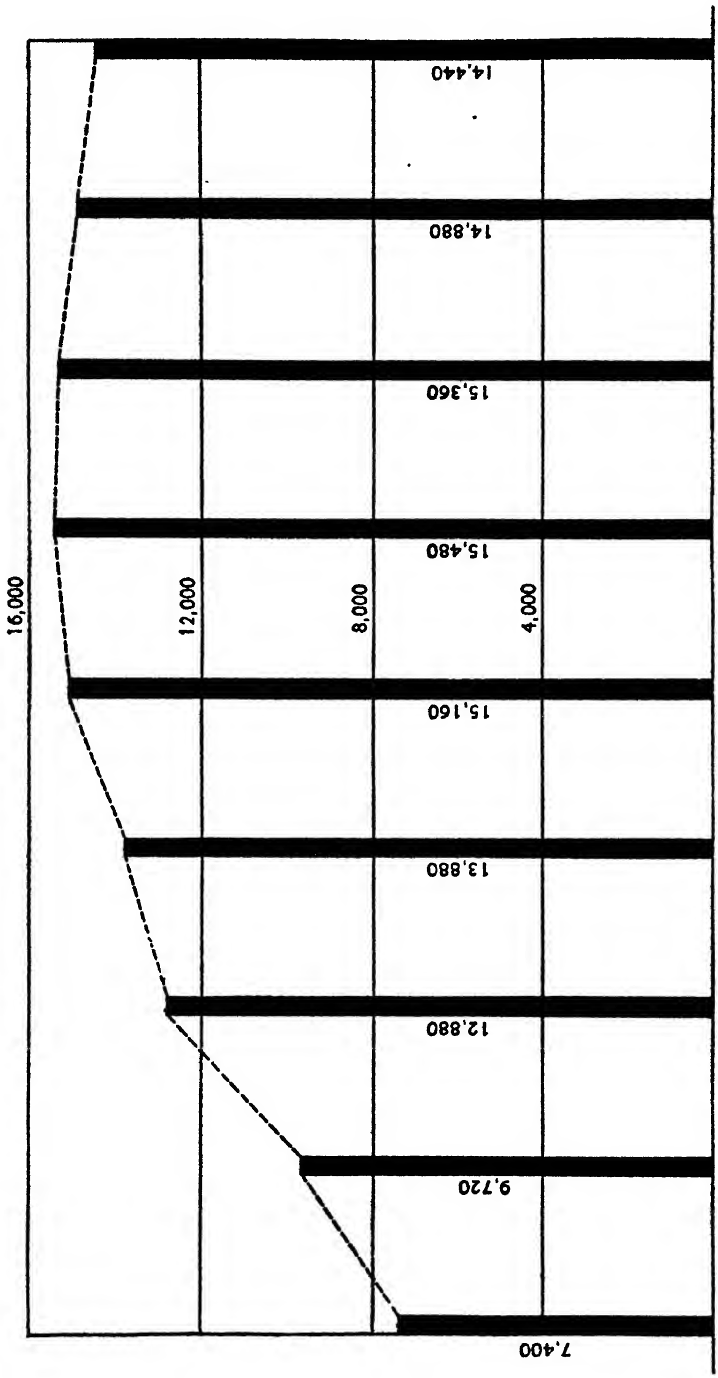
16,000
12,000
8,000
4,000
14,440
14,880
15,360
15,480
15,160
13,880
12,880
9,720
7,400

FIG.

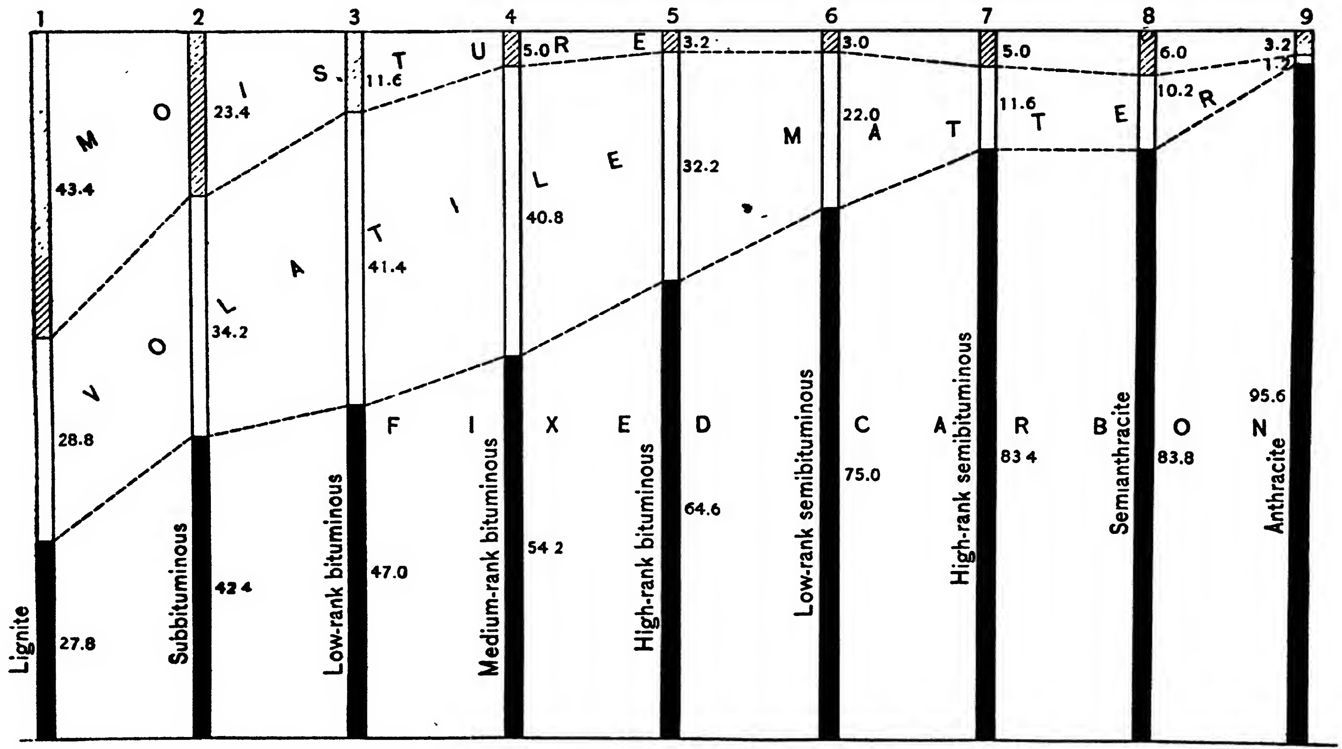

FIG. 1 (*b*).

FIG. 1.—CHEMICAL COMPOSITION AND HEAT EFFICIENCY OF THE SEVERAL RANKS OF COAL. (*a*) COMPARATIVE HEAT VALUE OF THE SAMPLES OF COAL REPRESENTED IN (*b*) COMPUTED ON THE ASH-FREE BASIS; (*b*) VARIATION IN THE FIXED CARBON, VOLATILE MATTER, AND MOISTURE OF COALS OF DIFFERENT RANKS COMPUTED ON SAMPLES AS RECEIVED ON THE ASH-FREE BASIS.

tabulation of a large number of ultimate analyses of coal, White[6] concludes that

except in the presence of unusual variations of hydrogen or sulfur, the efficiencies (calorific values primarily) of the coals, if ash be constant, rank nearly in the order of the ratios C:O, which in each kind of coal mark the progress of coal formation under dynamo-chemical influences.

Parr[7] uses this relation in proposing, as chemical criteria for the rank of a coal, the calorific value and percentage of volatile matter of the pure coal substance. His proposition takes care of that portion of the rank scale (low-rank bituminous coal, subbituminous coal, and lignite) where there is no significant variation in the total volatile matter but a marked increase in the proportion of CO_2 and H_2O in it due to the large proportion of oxygen in the coal. The method has further practical merit in that it does not involve ultimate analyses, which are infrequently made in technical laboratories. In America, most technical coal laboratories are now equipped with reliable calorimeters. It is evident, then, that our proximate and ultimate analyses of the coal aggregate can be correlated, to a certain extent, with the dynamo-chemical stages in coal formation, and is of considerable use in technical evaluation of coal; yet such analyses fail to differentiate many important characteristics and, in themselves, have not advanced our knowledge of the chemistry of coal beyond the empirical stage.

The Banded Constituents of Bituminous Coal

The alternating bright and dull bands in many bituminous coals have, for years, occupied the attention of investigators of the constitution of coal. Stopes,[8] in England, proposed the names of "vitrain," "clarain," and "durain" for these bright and dull bands, and the name "fusain" for the powdery charcoal-like layers found on some of the cleavage planes of many bituminous coals, called "mother of coal" or "mineral charcoal" by other writers.

Durain is the name given to the dull bands, and clarain and vitrain to the bright bands; the principal distinction between clarain and vitrain is that the vitrain has a more brilliant, glassy luster and is more vitreous fn structure than clarain. Under the microscope, vitrain is said to be oi uniformly structureless texture; that is, no plant structure other than perhaps a few isolated spores or strips of durain. Thiessen, however, has been unable to confirm these observations with respect to the structureless nature of the glassy bright coal bands. He has always

[6] David White: The Effect of Oxygen in Coal. Bur. of Mines *Bull.* 29 (1911) 70.

[7] S. W. Parr: The Classification of Coal. *Ind. & Eng. Chem.* (1922) **14**, 920.

[8] M. C. Stopes: On the Four Visible Ingredients in Banded Bituminous Coal. *Proc. Royal Soc.* (1919) **B-90**.

found typical plant-cell structure in all bright coal bands; it is, therefore, a question whether there is any real difference in the structure of clarain and vitrain—it may be a question of technique in preparing thin sections and observing them under the microscope. At least the names clarain, durain, and fusain seem acceptable for the visible portions of banded bituminous coal heretofore known as "bright coal," "dull coal," and "mother of coal."

Thiessen[9] has introduced the terms "anthraxylon" and "attritus" for classifying the ingredients of coal as shown by microscopic examination. Anthraxylon is the undisintegrated coalified wood that shows the typical cell structure of wood. He has shown that the bright coal bands are essentially anthraxylon, being the coalified trunks, branches, and twigs of trees that were buried in the peat debris.

Attritus consists of highly macerated plant debris and, under the microscope, shows recognizable remains of leaves, bark, cuticle, spore and pollen exines, bits of plant tissue, all intermixed with resinous, carbonaceous, and mineral matter. The dull bands of coal are made up of strips of anthraxylon in a ground mass of attritus.

The terms used in England may, therefore, be harmonized if we consider durain as "dull coal" made up largely of attritus but containing more or less anthraxylon, and clarain as "bright coal" consisting principally of anthraxylon. It is not clear to American investigators where vitrain comes in, unless it is pure anthraxylon so completely coalified that the woody structure is recognizable under the microscope only in specially thin sections under the most favorable conditions of illumination. Furthermore, the fact that anthracite, a late stage in the coalification process, shows abundant structure when etched by a flame indicates that the characteristic woody structure is present in all coals of woody origin when the proper methods are used to bring it out. We have discussed these relatively new terms in coal constituent nomenclature because of the great desirability of coming to a common understanding in the further discussion of chemical treatment and separation of coal constituents.

Separation of Coal Conglomerate by Organic Solvents

One of the most promising methods of separating the constituents of coal into groups is by treatment and extraction with certain organic solvents, such as pyridine, benzol, phenol, chloroform, ether, etc. No coal or lignite dissolves completely in any of these solvents. Owing to the tendency of the extracted materials of coal to oxidize and polymerize it is extremely difficult, if not impossible, to follow through such separations to definite identifiable compounds with any degree of certainty

[9] R. Thiessen: Structure in Paleozoic Bituminous Coals. Bur. of Mines *Bull.* 117 (1920).

that the fixed compounds existed as such in the coal. Nevertheless, extraction with inert solvents is probably the best method of isolating some of the chemical compounds existing in coal in the least changed, if not in an unchanged, condition.

Among the most effective solvents for this purpose are pyridine and benzol under pressure. Bedson,[10] on extracting pulverized coal for several hours with boiling pyridine, obtained a dark brown solution, sometimes showing a green fluorescence. The amount of material removed by the pyridine varied from practically zéro, with anthracite, to 35 and 40 per cent., in good gas coals.

The extracted coal had little or no coking property. Following Bedson, Wheeler[11] and his associates introduced the method of separating coal constituents into three groups, termed alpha, beta, and gamma compounds, by extracting the coal first with boiling pyridine and then extracting the pyridine soluble portion with chloroform. They describe these compounds as follows:

Alpha product, insoluble in pyridine, is a brown powder that, on destructive distillation, does not fuse and yields gas and very small quantities of tar, which consist almost entirely of phenols.

Beta product, soluble in pyridine and insoluble in chloroform, is a brown powder and is only distinguishable from the alpha product by its solubility in pyridine.

Gamma product, soluble in pyridine and chloroform, has the appearance of a resin or lac and melts at 100° C. On destructive distillation it yields gas and tars, composed of olefines, paraffins, and naphthenes; no phenols are produced. The residue is well fused and coked.

Wheeler concludes that the alpha and beta products are derived almost entirely from cellulose, while the gamma product is derived from the resinous constituents of coal. Recent work by Fischer and Schrader,[12] however, furnishes very strong evidence that most of the cellulose disappears during the biochemical stage of coal formation and that the degradation products of lignin contribute to the larger portion of coal, the cellulose having been decomposed to methane, carbon dioxide, and water by the action of bacteria. Thiessen has arrived at the same conclusion as Fischer, from a study of the biochemistry of plant decay and observations of the changes taking place in some existing American peat bogs.

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[10] Bedson: *Trans.* N. Eng. Inst. Min. & Mech. Engrs. (1899) **48**; *Jnl.* Soc. Chem. Ind. (1908) **27**, 147.

[11] M. J. Burgess and R. V. Wheeler: *Jnl.* Chem. Soc. (1911) **99**, 649.
A. H. Clark and R. V. Wheeler: *Ibid.* (1913) **103**, 1704.
D. T. Jones and R. V. Wheeler: *Ibid.* (1914) **105**, 2562; (1915) **107**, 1318.

[12] F. Fischer and H. Schrader: Neue Beiträge zur Entstehung und Chemischen Struktur der Kohle. *Brennstoff-Chem.* (1922) **3**, 65.

Another important method for separating coal into three groups of constituents is the extraction with benzol at high pressure and temperature. Fischer[13] and Gluud have carried out this method on bituminous and brown coals with benzol at 275° C. under 55 atmospheres pressure. The residue was non-coking similar to the alpha and beta products of the pyridine-chloroform treatment. The extract contained the constituents responsible for the coking and swelling properties of coal when subjected to destructive distillation. These soluble constituents, which they called "bitumens," were separated by further treatment with petroleum ether into a soluble oily substance, which gave to the coke its cementing properties, and an insoluble hard waxy residue, which seemed responsible for the swelling of the coking mass.

In good coking coals, the bitumens melt at 300° to 350° C., and gradually decompose in part, giving off gases, the residual portion continually rising in melting point and eventually hardening into a firm dense coke. The porous, weak coke, produced by high-volatile gas coals, is attributed to the distillation of a large part of the bitumens from the coal as undecomposed volatile matter. The non-coking of lean coals is due to the decomposition of the bitumens in the coal before they have been heated to their melting temperatures.

Illingworth[14] has developed practically the same theory of coke formation based on the pyridine-chloroform separation. He ascribes the degree of plasticity of fusing coal to the amount of gamma or "resinic" (γ) components (soluble in pyridine and chloroform), and the melting point and viscosity of the melted gamma (γ) constituents. The physical properties of the resultant coke are determined largely by the temperature to which the coal is subjected in the coking process and the proximity of that temperature to the melting and decomposition temperature of the gamma constituents. He showed experimentally that approximately 400° C. was the coke-forming temperature of coals producing porous coke, and from 430° to 450° C. for coals producing dense coke; and that, in the carbonization of intimate mixtures of any two of the three coal components, alpha, beta, and gamma, at temperatures varying from 450° to 900° C., only those mixtures containing gamma substances were capable of giving a residue of a coherent nature. Illingworth estimates that the gamma compounds begin to melt at 200° C. and become fluid at 350° C., which is in agreement with the melting temperature of Fischer's "bitumens." Extraction methods of analysis will therefore serve as a guide in the selection of coals of the desired coking tendency or for the blending of coals to secure coke of the requisite density and strength for metallurgical purposes.

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[13] F. Fischer, *et al.*: *Ges. Abhand. Ztschr. Kennteis d. Kohl.* (1917–1922) **1–4.**

[14] S. Roy Illingworth: *Coll. Guard.* (1920) **119,** 1441; *Iron & Coal Trades Rev.* (1922) **104,** 575; *Fuel in Sci. & Prac.* (June, 1922).

Sinkinson[15] has shown that unsaturated hydrocarbon gases, particularly those containing triple bonds, when decomposed by heat yield a compact finely divided carbon which has strong cementing properties; doubtless this is the result of close packing and the large surface energy thus involved. He thinks therefore that cementation of coke may be caused by thermal decomposition of unsaturated gases in contact with the carbonaceous mass. It may be remarked, however, that the concentration of unsaturated compounds, even in low-temperature gases, obtained under high vacuum is so low that it is hard to conceive of their having great influence on coke cementation. If we include the unsaturated compounds of the tar and also of its degradation product, pitch, the writers are willing to concede that thermal decomposition of the unsaturated constituents may be the main factor in coke cementation. Unsaturated compounds are easily decomposed by heat.

The most elaborate attempts to separate and identify the constituent chemical compounds in the pyridine extract were made by Hofmann and Damm,[16] who extracted 500 kg. of an Upper Silesian bituminous coal, obtaining 10 per cent. of the weight of the coal in the extract, and by Pictet, Ramseyer, and Kaiser,[17] who extracted 5½ tons of a Saar coal with benzol and obtained, after further treatment of the benzol extract with petroleum ether, an oil resembling tar amounting to 0.25 per cent. by weight of the coal. In this oil they separated and identified a number of hydrocarbons, some of which they also found in the tar obtained by distilling coal in vacuo at low temperature.

Hofmann and Damm treated their pyridine extract with ether, washed the ether extract with alkali and acid to remove acids and bases, and then distilled the resultant neutral oils, which amounted to 16 per cent. of the pyridine extract or 1.6 per cent. of the original coal taken. These oils were then fractionally distilled and a number of saturated and unsaturated hydrocarbons separated and identified.

One of the writers of this present paper visited Doctor Hofmann's laboratory last summer and had the opportunity of seeing the substances that had been identified and the hundreds of other fractions that have not been carried through to completion. Such research requires a tremendous amount of painstaking and tedious work, much of which is of no avail because of the very small quantity of the final products obtained. Doctor Hofmann said he should have started with 5000 kg. instead of 500 kg. of coal for the initial extraction.

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[15] E. Sinkinson: Some Observations on the Transition of Coal to Coke. *Ind. & Eng. Chem.* (1925) **17**, 27.

[16] F. Hofmann and P. Damm: Mitt. Schlesischen Kohlen Forschungs Inst., Kaiser Wilhelm-Gesell. *(1922)* **1**, *115.*

[17] Amé Pictet, Louis Ramseyer, and O. Kaiser: On Certain Hydrocarbons in Coal. *The Gas World* (1917) **66**, 21.

Net Result of Research on Constitution of Coal by Extraction Methods

Stopes and Wheeler[18] sum up the net results of the researches with organic solvents as follows:

1. Evidence has been obtained of the presence in bituminous coals of small quantities of (presumably but little altered) resins extractable by ether.
2. Free hydrocarbons exist in small quantities in coal.
3. Whatever be the exact nature of its action, pyridine affords a means of resolving many coals in such a manner as to render subsequent chemical examination less difficult.

In the opinion of the authors there has also been opened a promising field for study of the coking properties of coals by the use of the pyridine-chloroform method and by the benzol-petroleum-ether method of isolating the probable coking constituents for further study.

Action of Chemical Reagents on Coal

The treatment of coal with powerful chemical reagents, such as strong alkalies, concentrated acids, and oxidizing agents, has been one of the earliest methods for partly breaking down the coal conglomerate and isolating organized structure for examination under the microscope.[19]

The action of alkalies, concentrated acids, and oxidizing agents is of particular interest because this treatment discloses the "humic" or "ulmic" nature of the bulk of material in coal, and its relation to the degradation products of the plant lignocellulose, as distinguished from the hydrocarbons, waxes, and resins that comprise the gamma products soluble in organic solvents.

When peat, brown coal, or lignite is digested in a solution of caustic alkali, a part of the material appears to dissolve, imparting a deep brown color to the liquor. On acidifying the filtered solution, the dissolved material separates out as a brown flocculent precipitate. This precipitated material has been given various names, the most common being "ulmic acid," "ulmin," "humic acid," "humin," and "humic substances." British writers have generally adopted the terms "ulmin" and "ulmic acid." Most French, German, and American writers seem to prefer the terms "humin" and "humic acid." The humins or ulmins are true colloids. Their constitution is not known; it is even doubtful if they are true acids. If we knew the chemistry of humins, lignin, and cellulose, we would know most of the chemistry of coal.

[18] M. C. Stopes and R. V. Wheeler: The Constitution of Coal. *Fuel in Sci. & Prac.* (1924) **3**, 67.

[19] M. C. Stopes and R. V. Wheeler: The Constitution of Coal. *Fuel in Sci & Prac.* (1924) **3**, 356.

The amount of humic or ulmic acid that can be extracted from coal gives a rough indication of its geological rank. Thus 50 per cent. or more of peat will dissolve in alkalies; a much smaller proportion of brown coal and lignite, but yet enough to give a deep brown solution; while practically nothing is dissolved from true bituminous coal and anthracite. It is possible, however, to liberate the humic matter in high-rank coals by first treating them with oxidizing agents, as nitric acid; they will then color alkaline solutions brown. Slow atmospheric oxidation or "weathering" has the same action.

Action of Oxygen under Pressure

Fischer[20] and associates have recently published a number of articles on the action of oxygen under pressure (40 to 53 atmospheres and 200° C.) on plant constituents and the younger coals (brown coals) in water suspension with and without the presence of alkalies. They found that:

1. Cellulose, in the presence of water and alkali, at normal temperature and pressure of oxygen is converted into oxycellulose.
2. Cellulose, in the presence of sodium carbonate and water, at 200° C. and 40 to 53 atmospheres of oxygen is decomposed with the formation of lower fatty acids, as oxalic, fumaric, succinic, and traces of acids containing the furan ring.
3. Lignin is oxidized, in the presence of alkali, by air under pressure (200° C., 43 to 50 atmospheres) to aromatic acids among which are, mellitic, pyromelletic, isopthalic, and benzoic acids.
4. Resins and waxes are partly saponified by heating under pressure (200° C., 40 to 43 atmospheres) with alkalies.
5. Brown coals are oxidized by air or oxygen under pressure (7 hr. at 200° C.) in the presence of alkalies to aromatic acids principally, as takes place with lignin.
6. Similar pressure oxidation of bituminous coal gave 40 per cent. of non-volatile organic acids, one-fourth of which were identified as aromatic acids, benzoic and phthalic acids amounting to 12 per cent. of the weight of coal taken.

Fischer advances these results in support of his theory that the humic products in coal come from the lignin of the plants rather than from the cellulose. However, a number of other investigators are not ready to accept the lignin theory. In summing up the subject of the ulmin compounds in coal, Stopes and Wheeler consider the most rational theory at present is that both cellulose and lignin, together with the plant proteins, contribute to the formation of the ulmins or humins.

Action of Reducing Agents on Coal

As early as 1869, Berthelot[21] found that carbonaceous matter, such as wood, could be largely converted into saturated hydrocarbons by heating to 280° under pressure in a water solution of hydroiodic acid.

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[20] F. Fischer, *et al.*: *Ges. Abhand. Ztschr. Kenntn. d. Kohl.* (1920) **4**, 8, 343; (1922) **5**, 141, 135, 235, 292.

[21] Berthelot: *Ann. Chim. Phys.* (1870) **20**, 516.

Even carbonized residues were attacked, provided they had not been heated to so high a temperature during carbonization that their hydrogen was practically all driven out. Recently Fischer and Tropsch[22] verified Berthelot's results. They also succeeded in hydrogenating coals by heating with sodium formate and water in an autoclave at 400° C. The yields of ether-soluble oils were for the different ranks of coal as follows: anthracite, 1.6 per cent.; bituminous coal, 9.2 to 39.2 per cent.; brown coal, 26.8 to 45 per cent. Good results were also obtained by heating to around 400° with carbon monoxide and water under pressure. As to the question of what part of the coal was attacked to the greatest extent, Fischer concludes that the constituents derived from lignin were most strongly attacked. Brown coals that were poor in bitumen gave the largest yields, indicating that the bitumens were less attacked than the humic matter. He believes, therefore, that the products are, to a large extent, aromatics but has not proved this.

At the present time, the action of hydrogen on coal at high pressures and moderately high temperatures is being studied in a number of European laboratories. Bergius[23] heats coal suspended in oil, in a steel container to about 400° C. under hydrogen pressure of 100 to 150 atmospheres. By this treatment he claims to convert 80 per cent. or more of the coal into oils. Not much information is given as to the nature of the oils obtained, but it is presumed[24] that they consist of phenols and hydrocarbons, the latter being similar to those obtained from petroleum. Bergius' results have not been entirely confirmed, so far as the authors know.

Shatwell and Graham[25] have recently published a preliminary report of hydrogenation experiments by the Bergius method conducted at Birmingham University. They failed to obtain any more than 3 or 4 per cent. of the coal in the form of liquid products when bituminous coal unmixed with oil or phenol was treated at temperatures up to 425° C. and pressures up to 150 atmospheres. But when the coal was charged into the autoclave mixed with petroleum or phenol, they obtained liquid products in amounts up to 40 per cent. of the coal. Part of this liquid product was oil formed from the coal but most of it was in a form dissolved in the oil or phenol. They have not reported on the nature of the chemical compounds in the liquid products.

A significant conclusion from Shatwell and Graham's work is that the yields of products from the "clarain" and "durain" are approxi-

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[22] Franz Fischer and H. Tropsch: Die Umwandlung der Kohle in Öel, Gebrüder Borntraeger, Berlin, 1924. *Geo. Abhand. Zeitschr. Kenntnis. d. Kohl.* (1924) **5**.

[23] German patents Nos. 301231; 303893; 309282.

[24] F. Fischer and H. Schrader: *Brennstoff Chem.* (1921) **2**, 161.

[25] H. G. Shatwell and J. I. Graham: The Hydrogenation and Liquefaction of Coal. *Fuel in Sci. & Prac.* (1925) **4**, 25.

mutely the same and that the liquids obtained gave almost identical analytical figures. This corroborates other evidence that much the larger proportion of the chemical compounds in the durain and clarain—that is, the dull and bright bands—is the same.

Destructive Distillation of Coal

When coal is heated in a retort without access of air, the chemical compounds composing the conglomerate are broken down and probably react, to some extent, with one another, forming gaseous, liquid, and solid products. The proportions and nature of these products vary with the rank and kind of coal and also with temperature, pressure, and rate of heating. If the distillation is conducted very slowly in vacuo at a gradually rising temperature, the vapors suffer much less decomposition from secondary reactions than when conducted at high temperatures (1000° to 1200° C.), such as are used in gas and coke-works practice.

Low-temperature distillation of coal in vacuo, therefore, affords another method of attack in the problem of the constitution of coal, although it must be recognized that the products obtained are practically all the results of reactions taking place in the coal conglomerate as a result of heating rather than a distillation of these compounds out of the coal. The object is to avoid secondary reactions as much as possible in order to get primary products that may be traced back to the original coal compounds.

As pointed out in the beginning of this paper, the amount of volatile matter obtained from coals decreases as the rank of the coal increases. It has likewise been shown that the temperature at which the rate of evolution of volatile matter increases rapidly rises as the rank of the coal increases, from about 230°, with brown lignites, to 350° to 400° C., with anthracites. Also the composition of the gases given off varies in a fairly regular manner with the rank. The percentage of CO_2, CO, and H_2O decreases, and the percentage of CH_4 increases from lignite to anthracite. This variation would be expected from the progressive decrease of oxygen as the rank increases.

In general, the low-temperature distillation (up to 475° C.) of bituminous coals in vacuo yields tars consisting roughly of:

Constituents	Per Cent.
Unsaturated hydrocarbons	35 to 50
Naphthenes and liquid paraffins	35 to 45
Higher phenols (no carbolic acid)	10 to 50
Aromatic compounds	0 to 10
Solid paraffins	A little
Benzene, toluene, anthracene, naphthalene	Absent

Jones and Wheeler[26] distilled separately, in vacuo at low temperatures, the alpha, beta, and gamma constituents of coal. The alpha and beta constituents yielded very small quantities of liquid products consisting mainly of phenols. The gamma constituents yielded 40 to 50 per cent. of distillate below 400° C., consisting of paraffins, olefines, and naphthenes; there were no phenols present.

The separation of the coal conglomerate by pyridine and chloroform, therefore, offers one means of grouping into certain classes of constituents, in part at least, before distillation and gives a better chance to trace distillation products back to their parent coal compounds.

Strache[27] sums up the effect of destructive distillation on plant substances, peat, lignite, and coal as follows:

1. Cellulose is not decomposed by heat under 100° C.; at 270° C., it begins to decompose with such strong evolution of heat that the temperature immediately rises to 350°. The primary tar is easily decomposed by heating too rapidly; however, by careful heating even at atmospheric pressure a yield of 24 per cent. can be obtained. Much carbon dioxide and water are evolved with the tar. The tar contains neutral oils and phenols in considerable amount; acetone, furan derivatives, and acetic acid, but no methyl alcohol. In vacuo, levoglucosan is formed and is distilled over.

2. Lignin yields approximately one-half as much tar and one-third as much water as cellulose. The amount of neutral oil in the tar is considerable and the amount of phenols and acids is much greater than with cellulose. Contrary to cellulose, lignin tars contain methyl alcohol. Following is a comparison of cellulose and lignin tars:

Constituents	Composition of Tar From	
	Cellulose, Per Cent.	Lignin, Per Cent.
Neutral oils	31	13
Phenols	8	34
Acids	9	16
Water soluble organic matter	52	37

3. The resins, hydrocarbons, and waxes, extractable from bituminous coal are partly distillable unchanged, and partly broken down into hydrocarbons of lower molecular weight, some of them being unsaturated.

The bitumens in coal are the source of most of the tar and high heating value gas.

4. The humic acids yield on destructive distillation, an insignificant amount of tar but much gas and solid residue. The distillation products (tar) contain much acetic acid and tar acids. No paraffin is present.

[26] D. T. Jones and R. V. Wheeler: The Composition of Coal. *Jnl.* Chem. Soc. (1915) **107**, 1318

[27] H. Strache and R. Lant: Kohlenchemie. Akademische Verlagsgesellschaft M. B. H., Leipzig (1924) 552.

Wheeler[28] and his associates state that they: "hope to be able ultimately to correlate with definite morphological tissues or portions of tissues of the original coal plants, specific chemical substances now in or yielded by coal." For example, they have obtained a quantity of pure cuticle, freed from the debris of the coal substance, sufficient to allow of a study of its behavior under different modes of heat treatment; from which the products of its destructive distillation can be determined and possibly its chemical constitution deduced.

Conclusion

In conclusion we may say that the modern views of the chemistry of coal take cognizance of the conglomerate and colloidal nature of coal. Microscopical examination has shown the presence of more or less altered plant remains in coal of all ranks. The difference in structure of the "bright" and "dull" bands of bituminous coal has been definitely shown. The bright coal is principally anthraxylon, the dull coal is largely attritus often containing small strips of anthraxylon; these are structural differences.

The best-known chemical method of resolving coal into groups of compounds is by extraction with pyridine, followed by a subsequent extraction of the pyridine soluble portion with chloroform. The pyridine appears to act partly as a dispersing agent of the coal colloids and makes them accessible to the solvent action of the chloroform. The chloroform extract, or gamma fraction, contains the hydrocarbons, waxes, and "resinic" compounds. These appear to include the cementing constituents and those that cause swelling in coke; likewise the compounds that yield the paraffins, olefines, and naphthenes in the liquid products of carbonization of coal. The alpha and beta fractions contain the bulk of the ulmic or humic products in coal. These products contain small percentages of nitrogen and organic sulfur.

The question of whether the coal humins come from cellulose or lignin is not settled. The earlier theory that cellulose was the principal contributing factor seems untenable. Recent chemical research tends to favor the theory that lignin is the principal source. More light is needed on this question by further research on the earlier stages of coal formation, namely a study of peat taken from bogs at various depths and a study of the brown coals and lignites.

We hope that investigators (those in America, in particular) will carry on this work because America is so richly endowed with coal deposits of many types and ranks, thus providing an unusual opportunity for applying the newer chemical methods developed by European investigators to the correlation of constituents through the various stages of coalification.

[28] M. C. Stopes and R. V. Wheeler: The Constitution of Coal. *Fuel in Sci. & Prac.* (1924) **3**, 133.

DISCUSSION

S. W. Parr, Urbana, Ill.—I wonder if we appreciate what a transformation has been going on in the methods of the study of coal. One thought that comes to mind is where will be the proper place to start a reform in the matter of nomenclature? If we do not do that pretty soon, a reformation will be beyond hope. The vitrain, clarain, durain advocates are getting their terms well established in their country, while lots of us do not agree on these terms. May I ask if pyridine is altogether satisfactory? The criticisms were that it was not a true solvent, but a reagent; is it satisfactory from the standpoint of possible increase of nitrogen compounds in the extract? We have been shying at the use of pyridine, but our foreign brethren seem to adhere to it. The use of an oxidizing fluid is very pronounced and the assumption is that that is on the cellulose residue and not on the lignite.

David White, Washington, D. C.—It has been my feeling that had the coal fields in Great Britain belonged to diverse geologic periods, as is the case in this country, with extensive deposits and production of lignite, subbituminous, and bituminous of different ranks, the British point of view and conclusions as to the four "ingredients," and even as to the general evolution of coals, would be different from what they are now. Surely "vitrain" would not have come into use had the wood been followed from peat through its history. We see these jet-like lenses and layers—sometimes thick deposits—in anthracite as well as in coals of lower ranks; and sooner or later some one develops the right sort of slicing and illumination to bring out the fact that they are transformed wood or other plant tissue. Typical vitrains have been found by Doctor Thiessen to consist of wood transformed or, really, impregnated by humic (ulmic) matter. If the chemical deductions based upon "vitrain" by the British research investigators are true of the vitrain which is known now to consist of wood, then the vitrain, if there is such, that does not consist of wood, possesses apparently the same chemical features, and, chemically, loses its value as an ingredient, so-called, of coal. It is conceivable that we have in swamps precipitation of ulmic or humic acid material at times. None of us, I think, will dogmatically deny this. Yet, that it comprises what is commonly termed vitrain is strongly and persistently to be denied.

The evolution of coal seems to be regarded by our British colleagues with very great caution. They seem unwilling to commit themselves to the proposition that coal is the product of the progressive evolution of swamp deposits, originally peats. Doctor Fieldner has spendidly reviewed the question both chemically and paleontologically. The original deductions from field geology are conclusive; it is very gratifying

to find them fully corroborated from the other two standpoints,—the microscope and the chemical laboratory.

The term "rank" as applied to coal was, I believe, first introduced in the Geological Survey to replace "grades," which was equivocally used. A low-grade coal might be a high rank coal that was very dirty, or it might be a lignite.

The choice of a word imposes the obligation to take a word not misused in the particular application or field. "Rank" seemed to meet the requirements. Rank, however, implies a degree of precision, or fixity, that is slightly misleading, but I do not know a better word. The difficulty lies in the complete intergradation from rank to rank within a group or division of coals, such, for example, as semibituminous.

"Anthraxylon" does not appeal very strongly; vitrain is entirely superfluous and should go overboard. Is there a word we can substitute for them that is either common English or that, defining itself, will be understood?

REINHARDT THIESSEN, Pittsburgh, Pa.—The word "xyloid" has been used for lignite; lignatoid is a word used by others. But a study of the literature shows great objection to these words. Finding that these residues in the coal were derived definitely and absolutely from the woody substances of plants, I sought diligently for a word, and consulted many scholars in various languages. I finally took "anthrax," the Greek word for coal, and "xylon," the Greek word for wood, and combined them into "anthraxylon" meaning woody coal. I do not like the word any too well myself and have said so from the start. It is too long, too bunglesome, and too hard to pronounce, yet I could not find a word that would express the same meaning. In the meantime our English contemporaries introduced their words, which mean no more than our old words, dull coal and bright coal. Those words have been used for years and are so thoroughly embodied in our literature that they can not be ignored, so I never paid any attention to these new words, durain, clarain and vitrain.

My observation during the last years shows that by far the larger part of the anthraxylon, those parts of coal derived from wood, are largely derived from the lignin in wood, but not entirely.

A. C. FIELDNER.—All methods of extracting coal by solvents have certain disadvantages. For example, pyridine leaves some residual nitrogen in the insoluble residue. It is a question of whether this is simply small amounts of adsorbed pyridine or whether pyridine combines with certain constituents of the coal. Recent work by Pearson[29] proves that the action of pyridine is not wholly direct solution but to some extent dispersion, a fact that has been suspected for some time. Pearson has demonstrated the colloidal nature of pyridine solutions of coal. Pyridine

[29] A. R. Pearson: *Jnl.* Soc. Chem. Ind. (1923) **42**, 68T.

has the strongest action of any of the commonly used solvents for resolving coal into different groups of constituents; as high as 20 to 35 per cent. may be extracted.

Benzol extracts but a small percentage of coal at ordinary temperatures; at temperatures of 200° to 280°, it extracts more. Franz Fischer obtained as high as 8 per cent. on certain German coals. Decomposition of the coal, due to the high temperature, may have aided in making more of the coal soluble in benzol. This same question applies to the action of high boiling solvents like quinoline. The investigator has, therefore, to choose between two evils—either pyridine at a low temperature with possible combination of certain constituents, or solvents at high temperatures in which some decomposition may have occurred due to the action of heat.

Clarence A. Seyler, Swansea, Wales.—I am particularly interested in the discussion of the term "anthraxylon." I think the word is a good one to express Doctor Thiessen's conception that all bright coal is derived from lignified tissue, though I imagine that cortical tissues must be included as well as xylem. Without further investigation, it is impossible to be certain of the relation between anthraxylon, vitrain, and clarain, as used by Doctor Stopes. I think Doctor Stopes's terms clarain and vitrain make a useful distinction between the bright glassy coal and that which has a silky luster, while durain and fusain distinguish two kinds of "dull coal." These terms, like alpha, beta, and gamma compounds, do not commit us to any theory of the nature or origin of the substances.

Note.—As the result of Doctor Thiessen's kindness in instructing me during my visit to Pittsburgh (after the Meeting) in his technique, I am able to apply it to British coals and to compare it with the method of etching polished surfaces. I hope shortly to be able to come to a definite conclusion on the matter and trust that we may reach an agreement on the use of the terms.

Contact Metamorphism of Some Colorado Coals by Intrusives*

By J. Brian Eby,† Washington, D. C.

(New York Meeting, February, 1925)

Contact metamorphism of coals is any physical or chemical change in the character of a coal directly attributable to heat of surface or intrusive igneous rocks. Coal beds so affected are found in the United States, England, Alaska, Mexico, New Zealand, Greenland, and other countries. Particularly in the United States, there is a wide occurrence of contact altered coals; conspicuous examples are found in Colorado, Utah, New Mexico, Illinois, and North Carolina.

During a recent examination of coal beds on Yampa River, in northwestern Colorado, the author had an opportunity to make some detailed observations on the contact metamorphism of coals. In this field, coals over an area of 20 sq. mi. have been affected by dikes, sheets, and sills;[1] samples of the coals were systematically collected and analyzed,[2] with the view of obtaining more specific data on the character of these alterations. The investigation was threefold in purpose: to secure information on the lateral effects of a dike cutting a coal bed, on the range in vertical effects on coal beds overlying sheets or sills, and on the range in the vertical effects on coal beds underlying sheets and sills. Favorable field conditions, such as fresh outcrops and newly dug prospects, made possible many of the field observations and collections.

The coals studied in this field belong chiefly to the Mesaverde and "Laramie" formations. The Mesaverde coals, on the average, are blocky low-rank bituminous coals; the "Laramie" coals, which are considerably younger, are of subbituminous rank. The coals of both formations, in the northeastern part of the Yampa field, have been greatly affected by basalt intrusives, yielding all variations of carbonized coal from natural coke to the unaffected material.

The igneous rock that directly affects the coals is a fine-grained olivine basalt that is intruded, in sheets up to 200 ft. thick, into the coal-bearing

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* Published by permission of the Director of the U. S. Geological Survey.

† Assistant Geologist, U. S. Geological Survey.

[1] H. S. Gale and N. M. Fenneman: The Yampa Coal Field, Colorado. U. S. Geol. Survey *Bull.* (1906), 297.

[2] All analyses were made by the Bureau of Mines.

formations. These sheets have given rise to many small vertical dikes and are themselves offshoots from one or more of the large massive plugs that make the topographic features of Pilot, Hooker, and Wolf Mountains.

Lateral Effects of Contact Metamorphism

Six samples of coal were collected in one 300-ft. prospect entry on the Crawford tract of the Moffat Coal Co. The entry ended abruptly against a 25-ft. diabase dike. The percentage of fixed carbon for each sample computed on the "pure coal" basis and the relative distances of each sample from the dike are shown in Fig. 1. The curve connecting

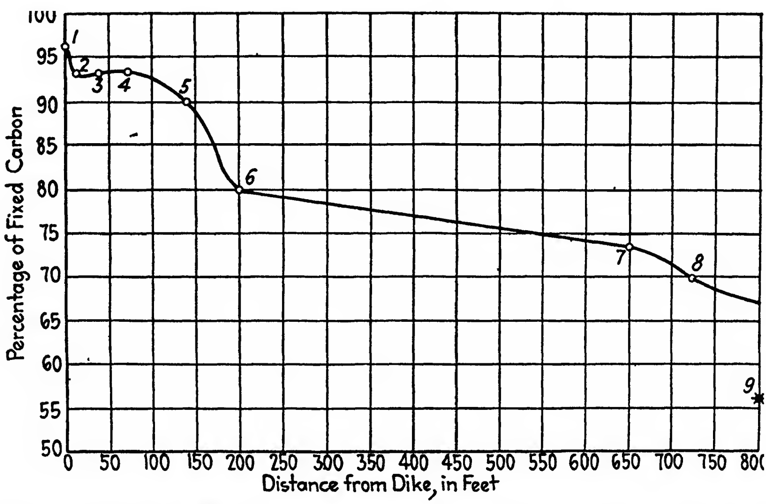

Fig. 1.—Percentages of fixed carbon in a coal bed as determined by eight analyses of samples collected at varying distances from a 25-ft. dike; coal bed is underlain by a sill; at 9 is shown average of 56 samples of unaffected coals. All analyses are computed on moisture- and ash-free basis.

the points, therefore, represents the amount and trend of the carbonization of the coal bed at and near the dike. The shape of the curve, however, is the result of the combined effect of the dike and a sill, about 50 ft. thick, that is estimated to underlie the coal bed from 50 to 60 ft. The effect of the sill on the curve is discussed later. In view of the presence of the sill, the effect of the dike alone cannot be definitely proved by the curve. It strongly suggests, however, that the effect of the dike does not extend beyond the locality of sample No. 2, or beyond 15 ft. A sample collected in a nearby entry several hundred feet from the dike but in the same relative position to the sill shows a fixed carbon content of 92.0 per cent. (Lab. No. A-3039), indicating that the sill without the dike is capable of carbonizing a coal bed to the rank shown by samples No. 2 to 5 in the curve. If it were not for the sill, it is believed the curve would

be L shaped—dropping almost vertically from 2 to about the level of 9 and then trending horizontally toward 9, which represents the average fixed carbon percentage (moisture- and ash-free basis) of 56 samples of the unaffected bituminous coals of the region.

The aureole of coking at the contact of the coal bed and the dike extends from 16 to 20 in. into the coal bed from the actual contact. The coke is jointed into irregular hexagonal fingers from ¼ to ¾ in. thick, which parallel in general the bedding planes of the coal bed.

Samples of the coke and adjacent coal were collected and tested for porosity and density;[3] the results of these tests are listed in Table 1, together with three other tests for comparison:

TABLE 1.—*Porosity and Density Tests of Coal and Coke*

	Porosity, Per Cent.	Density	Remarks
Coke, artificial	45.5	1.823	Beehive coke given for comparison.
Coke, natural	23.6	1.500	At contact of dike and coal bed.
Coke, natural	9.8	1.472	At edge of aureole and uncoked coal.
Anthracite	6.0	1.503	Coal anthracitized by underlying sheet.
Bituminous	8.5	1.383	An average sample of low-rank Yampa bituminous coal.
Subbituminous	15.47	1.426	An average sample of Yampa subbituminous coal.

The porosity determinations given are of lump samples about ¼ in. on the three sides, and the density determinations are of the materials making up the samples. The actual contact coke shows a porosity only one-half that of artificial coke. The porosity decreases rapidly to a minimum at the anthracite rank and then rises to over 15 per cent. in the subbituminous rank. It is interesting to note that the porosity of the subbituminous coal is considerably greater than that of the natural coke at the edge of the aureole but much less than that of the coke at the contact.

The conditions in the coke oven and at the contact of a dike and coal bed are widely dissimilar and comparisons of the products are doubtless of more interest than value. Temperatures in coke and byproduct ovens range from 950° to 1200° C.; the melting point of some of the basalts ranges from 1200° to 1300° C. Thus, while temperatures are somewhat comparable the differences in pressure and the initial character of the

[3] By A. F. Melcher, Associate Geophysicist, U. S. Geological Survey. Methods used in making the tests were similar to those for oil and gas sand samples. They were described in *Bull.* Amer. Ass. of Pet. Geol., November-December, 1924.

coals, more than the temperature, are thought to account for much of the dissimilarity between artificial and natural coke. In the oven, the the material is coked at atmospheric pressure and expands freely, providing the large percentage of pore space shown in the table. In expanding, the material is permitted to become more thoroughly carbonized and the density of the coke grains is increased over that of the natural coke. At the contact of the dike and coal bed, the coal is under great pressure (both from the overlying rocks and the intrusion of the dike), expansion is prevented, and a less porous coke is formed. Probably because the natural coke is less porous, carbonization is less complete and the grains of the coke are not as dense as in the artificial variety.

Vertical Effects of Contact Metamorphism

Samples of coals occurring above and below igneous sheets were collected to show the vertical range in the effects on coal beds of heated

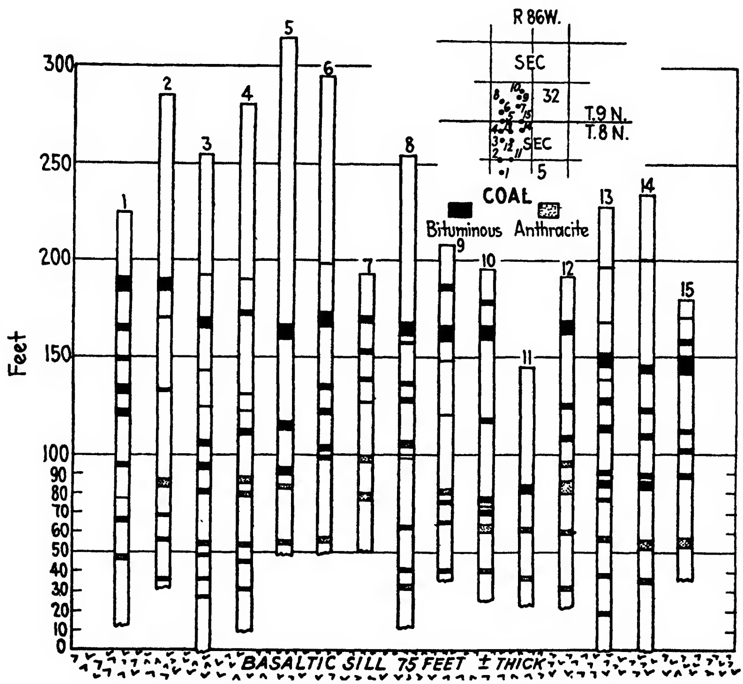

Fig. 2.—Logs of bore holes prospecting for coal beds over a 75-ft. sheet; the anthracite of the drillers is all coal showing effects of the sill.

rock masses. Fig. 2 is a correlation chart of logs of 15 holes put down to prospect for coal lying above a sheet from 75 to 100 ft. thick. The differentiation between anthracite and bituminous coal in the case of these logs was made by drillers and should be understood to mean only a

recognizable change in the character of the coal beds. The upper limit of this observed effect ranges from 60 to 110 ft.

The lowest coal shown in log 5 was sampled in a short prospect entry. The analysis (Lab. No. A-3051), on the pure coal basis, gives 84.3 per cent. fixed carbon for a fuel ratio of 5.36; this coal is of average semianthracite rank. The coal bed occurring 60 ft. above the semianthracite bed, in log 5, was also sampled and analyzed (Lab. No. A-3050); it showed 58.1 per cent. of fixed carbon for a fuel ratio of 1.38; this coal is of average bituminous rank. The coals in Fig. 2 shown within 50 ft. of the sill were not exposed and samples could not be collected.

Fig. 1, showing percentages of fixed carbon for samples 1 to 8 (Lab. Nos. A-3042–3047 and A-3035–36), illustrates the effect of an underlying sheet. Samples 2 to 5 are anthracitized by a sheet that is estimated to underlie the coal by about 50 to 60 ft. Sample 6, taken close to the mouth of the prospect entry, does not represent a fresh coal, but 7 and 8 are fresh samples. The gradual decline in the carbon content from 4 to 8 may be interpreted either as due to the thinning of the sheet and the lessening of its effect or to an increased distance from the sheet. As the direction, on the ground, of the decline in fixed carbon content is from northeast to southwest, which coincides closely with the direction from the source of the sill to its feather-edge, the former interpretation is more likely to be correct.

Two samples of coal were collected and analyzed from beds underlying a large sheet. In upper Elkhead Canyon, two coal beds outcrop at 26 and 42 ft., respectively, below a sheet 200 ft. thick. The bed 26 ft. below the igneous rock contains, on the pure coal basis, 92.8 per cent. fixed carbon for a fuel ratio of 12.88 (Lab. No. A-3166); this is a good anthracite. The coal 18 ft. lower contains 84.4 per cent. fixed carbon for a fuel ratio of 5.40 (Lab. No. A-3167); this is a semianthracite.

Summary

Igneous activity in the northeastern part of the Yampa coal field has locally affected many of the coal beds of this region. Samples of the coal were collected to throw some light on the character and range of the effects of these intrusions.

Analyses indicate that a 25-ft. dike is limited, in its effect on a coal bed, to a distance of about 15 ft. Megascopic examination of the bed fails to reveal an observable effect for a lateral distance of more than 20 in. In a vertical direction, a sheet 75 ft. thick has affected coals up to an average of 80 ft. above the sheet. Analyses show that true anthracite is formed at least as far as 45 ft. above the sheet in this field and true semianthracite as far as 55 ft. above the sheet, provided the coals are not affected by dikes. It is also shown that a 200-ft. sheet or sill will alter to a true anthracite a low-rank coal occurring 26 ft. below the sheet; and to a semianthracite a coal occurring 44 ft. below the sheet.

DISCUSSION

Geo. C. McFarlane, Oak Creek, Colo. (written discussion).—I agree with the author that lateral contact metamorphism of coal does not extend far from contact. At the southeastern edge of the Yampa coal field, a dike of diabase 8 to 12 ft. thick cuts through a 12-ft. bituminous seam. The coking extended back 17 in. from contact; at contact, coke (ash and moisture free) showed 90.6 per cent. fixed carbon; 17 in. from contact, 65.4 per cent. fixed carbon; 36 in. from contact, 54 per cent. fixed carbon. This latter is the normal fixed carbon percentage for the seam; the normal ash content is 5.20 per cent. The coke at contact showed 10.20 per cent. ash; 17 in. away, 10.10 per cent.; and coal 36 in. away, 5.8 per cent. ash. This would indicate a coke yield of 56 per cent.

The metamorphism of coal seams by intrusive sills is much more interesting, as in the area studied by the author are commercial deposits of high-grade anthracite; metamorphosed from bituminous coal by intrusive basalt sills 40 to 90 ft. below coal seams.

On the Crawford tract, which is the original discovery and has the best showing of anthracite so far uncovered, there are two seams that have been carbonized by the basalt. The lower seam, which is nowhere over 3 ft. in thickness, is from 40 to 52 ft. above the sill and is, wherever opened, true anthracite with a carbon per cent. of 89 to 91. The upper, or big seam, is from 80 to 96 ft. above the basalt sill and in a distance of ½ mile shows every grade of coal from bituminous to anthracite. Over a large area, the bottom split of the seam is true anthracite and the upper split semianthracite. In places, there is a range of 25 in the fixed carbon percentage between floor and roof of seam.

As active prospecting is now under way, the prospect drift shown in Fig. 1 has penetrated the 25-ft. dike and has been extended 250 ft. beyond. The fixed carbon percentage has increased from 87.50, beyond the coke aureole, to 94.81 per cent., at face. The dike was determined as olivine basalt, the same as the sill. Beside the olivine basalt, there are three varieties of diabase dikes on the property. One variety is similar to the Pilot Mountain plug to the northeast and one variety, which is quite vesicular, is similar to the Wolf Mountain eruptive core to the southeast.

From a comparison of the size of the vein and its ash content at different points where it is pure bituminous, with the thickness of the vein and ash content where the vein is pure anthracite, it would appear that 100 lb. bituminous made 78½ lb. of anthracite. In the process the bituminous coal lost 21½ per cent. of its weight and 14 per cent. of its heating value, or 1730 B.t.u. per lb. On this basis and on the ultimate analysis of the bituminous and the anthracite, the volatile distilled off was about as follows: $4(CH_4) + NH_3 + 14(H_2O) + 7H_2$.

Assuming that the temperature of the intruded basalt was 1400° C. and that 60 per cent. of the heat radiated upward and 40 per cent. downward, and that the big coal seam, owing to the low heat conductivity of coal as compared with sandstone and shale, acted as a heat jacket, the 60-ft. basalt sill would heat a 200-ft. belt of rock. The highest temperature reached at the base of the big seam would be $^{60}/_{200} \times 1400°$ C., or roughly 420° C. Besides the heat of the basalt, all the occluded magmatic gases would collect under the base of the coal seam. These magmatic fluids, consisting probably of water, chlorine, fluorine, and nitrogen, no doubt played some part in the process. The wide variations in the metamorphism of the big seam would indicate that the difference in porosity of the intervening sandstones and shales might cause local concentrations of these fluids under certain areas of the seam and thereby stimulate the heat reaction. It would also seem that anthracite of a fixed carbon percentage of 94 is a definite chemical compound $CH_2C_2.C_2$. In this locality such anthracite would have an ash content of 8–12 per cent. and a specific gravity of 1.50–1.53.

The volatile matter given off by the coal during the carbonizing process is cut or cracked by the halogen and other reducing elements occluded by the cooling basalt. No doubt heat and a small quantity of water are enough to transform bituminous into anthracite. The anthracite crystallizes out of the pasty bituminous matrix like sugar out of syrup, only, in the absence of magmatic gases to act as exciters, the reaction requires more heat and heavier hydrocarbons are lost in distillation.

In one place where the basalt sill is apparently unusually thick, the seam shows an ash content of 17 per cent. and a density of 1.88. The seam is shrunk in proportion to its high ash content. The author's observation of a seam 42 ft. below a 200-ft. basalt sheet only being carbonized to semi-anthracite would also indicate fluids occluded by the basalt had a major part in transforming the bituminous seams.

From the known rate of conductivity of sandstones, shales, and coal, the time elapsing between the intrusion of the basalt and the cooling to normal temperature was short, not over 400 years.

W. T. Thom, Jr., Washington, D. C.—I would like to emphasize the point, brought out by the author, that water vapor or gas emanating from the sills is probably the major cause of the alteration of the coal, the heat radiating by conductivity of the rock being relatively of quite minor importance.

Progressive Regional Carbonization of Coals

By David White,* Washington, D. C.

(New York Meeting, February, 1925)

Attention has been given to the sources and supply of the raw vegetal matter and the conditions of its submission to the process of sedimentation. An original and most valuable review has been made of the more important or significant chemical compounds originally contained in the organic debris, and of the biochemical changes undergone by the latter during deposition. Consideration also has been given to the factors controlling the selective biochemical decomposition, in whole or in part, of this debris, and the deposition, as sediments, of the undecomposed plant structures and compounds, together with more or less of the so-called "ulmic," or "humic," organic decomposition products in colloidal solution.[1]

Biochemical Changes End in Peat Formation

The biochemical process terminates in the peat stage of coal formation, and with the cessation of this process organic sedimentation is completed. All subsequent changes result from geological causes and conditions. The deposits are in the form of peats of different types, organic muds, oozes, etc. They are essentially uncompressed and are wholly unconsolidated, and their water content is great, amounting to over 85 per cent. near the surface of the deposit. Many of the chemical compounds remain as in the once living organisms; others are biochemically broken down and new ones formed.

Geochemical and Geophysical Changes in Buried Deposits

Subsequent Changes "Dynamochemical"

The changes which subsequently take place through dehydration, lithification, and simultaneous progressive chemical alteration, by which organic sediments are advanced to brown lignite, subbituminous, bituminous, semianthracitic, and graphitic ranks, are geochemical and geophysical, and the process, which really is metamorphic,[2] takes place under dynamic influences. In fact, the essential changes, including loading,

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[1] See preceding papers in this volume.

[2] D. White: Bur. of Mines *Bull.* 38 (1913) 94, 127.

progressive dehydration, compression, induration, jointing, devolatilization, and refinement of cleavage, with gradual losses of carbon, hydrogen and oxygen, which characterize progressive carbonization, are now in progress in most coal fields. Recent organic sediments are being more deeply buried, compressive thrusts producing buckling, faulting, and earthquakes, are still in action. To the progressive transformation, under geologic conditions and forces, mainly dynamic, of the buried organic matter, the writer has applied the term "dynamochemical," in contrast with the biochemical processes which cover the first or peat stage of transformation of organic debris into coal or other carbonaceous sedimentary deposits.[3]

Ranks of Coal Not Due to Original Differences

It has been shown in other papers in this volume that the principal chemical compounds forming the plant substances have not changed from age to age of the coal-forming periods, notwithstanding the evolution meanwhile of families, genera, and species. Woody tissue in thick secondary development, spores, pollen grains, pith, cambium, bark, leaves, epidermis, cuticles, glands, wound secretions, pigments, protoplasm, starches, gums, waxes, oils, and resins were apparently as plentiful in the Mississippian as in Tertiary peats. No essential chemical distinctions that might notably affect the composition of the biochemical deposit have yet been detected. Bacteria and fungi were varied and numerous. The waxy-fatty algae forming the bogheads and entering many cannels of the early Carboniferous appear almost indistinguishable from those of the boghead forming today—a fact not remarkable in view of the simple structure and low order of these plants. In all late Devonian and younger coals we have woody or distinctly xyloid types; beds rich in fusain, and deposits formed largely of spores, resins or other hydrogenous debris. In fact, in their fossil components and original constitution, all coals, graphitic and anthracitic, bituminous and brown, have their counterparts in the peats and other organic sediments of the present day. The woody type or group, with much debris of stem, branch and twig, and more or less fusain, is the common type—the ordinary "humic" type—of coal in all coal fields, as well as of peats laid down in the temperate and warmer moist climates of the present day. Genuine peat like that of today but silicified before compression under loading, has been found in the lower Devonian of Great Britain. The revelations of the microscopical study of the coals themselves as described by Renault,[4] Bertrand,[5] Thiessen, Jeffrey, Turner, and others find confirmation in the peat samples preserved

[3] D. White: *Econ. Geol.* (1908) **3**, 292.

[4] B. Renault: Sur Quelques Microorganismes des Combustibles Fossiles. 1900.

[5] C. E. Bertrand: Conclusions Générales sur les Charbons Humiques et les Charbons de Purins. 1898.

in the calcitic and siliceous "coal balls" formed at or near the surface of the Carboniferous peats in certain districts of Europe and America.

Changes Due to Geologic Processes

It is further to be noted that in one region or another peats (coals) of the common (humic or woody) type, cannels, and carbonaceous muds are to be seen in every stage of advancement by alteration through the successive ranks up to graphites and graphitic slates. There is no known chemical distinction and no physical differentiation, other than paleontologic, between the anthracite or the bituminous coal of the Cretaceous and that of the Carboniferous, the Tertiary and the Triassic. These significant circumstances give basis for the conclusion that the successive ranks of the ordinary woody coals—which undoubtedly were of essentially identical constitution and chemical composition at the beginning—are stages in the progress of the evolution of these coals, an explanation that finds support both in the laboratory and in the field. Coals in the retort or experimental furnace may be further altered (carbonized) to products nearly similar to the coals of higher rank. On the other hand, in a single coal field the same bed of coal, preserving all its depositional features and characters of fossil constitution, is seen to change gradually from one rank to another in passing from one locality to another. This regional change in a continuous bed, without change in type, may be seen in most large coal fields. It is the result of progressive regional metamorphism.

Whether the organic substances laid down with the inorganic be much or little, structural debris, or humic solution, they form part of a sedimentary deposit never to be wholly obliterated in the course of subsequent dynamochemical changes. Carbonaceous residues will remain in the sediments. Once past biochemical action, wood cells and other tissues, together with exines, and algal cells, may later be reduced and even deformed or torn by pressure, and become shrunken by progressive losses of water, carbon, hydrogen, oxygen, and nitrogen, but the wasted vestiges will retain and define the original structure, even when completely carbonized. This has been satisfactorily shown in anthracite by Turner and Winter. Fusain is easily recognizable in the graphitic coal of Rhode Island, if the bed is not too badly crushed.

Progressive Carbonization as Observed in Different Regions

The United States offers unrivaled opportunities for the observation and examination of the progressive alteration of coal from rank to rank in a given direction within a single basin. In horizontal or slightly dipping formations its coal measures extend throughout great areas. Its territory embraces coal deposits of Mississippian, Pennsylvanian,

Permian, Triassic, Jurassic, Cretaceous, and Tertiary ages. In rank they range from peat to graphitic.

In connection with his studies of the Paleozoic floras and of the coals themselves, the writer has for nearly twenty years given some attention both to the contributions of raw vegetable matter from which the coals were formed and to the evidence of the progressive alteration, under geological conditions, of the deposits that is to be observed in the same formation and even in the same bed in passing from point to point, or from one side of the basin to the other.

This progressive alteration (metamorphism), or "carbonization," of the combustible organic matter in the deposit includes both the organic debris and the solidified decomposition products which form the binder of what was once peat or organic mud.

"Fixed Carbon" Used to Indicate Stage of Carbonization

The states in which the increasing proportions of carbon actually exist in the coal is unknown, and no exact method appears to have been employed or even devised for determining its amount. We are therefore compelled to fall back on the results of the very convenient, though inaccurate, unsatisfactory, even rather unscientific, "proximate analysis." However, far as the proximate analysis, with its incompatibilities, may lie from the ideal of chemical truth, it nevertheless furnishes a scale indicating the amounts of conventionally accepted "fixed carbon" in the coals of middle bituminous and higher ranks, though it leaves great lack of information as to the progress of carbonization in the coals of lower ranks.

In the coals below (as well as above) the middle bituminous rank the progressive evolution or carbonization of the fuel is closely indicated by the decrease of oxygen (ash and moisture-free basis) in the coals, or by the ratio of such oxygen to the total carbon.[6] Unfortunately, the application of this method requires "ultimate" analyses, which may not be at hand.

Since our interest relates only to the carbonization of the organic combustible matter in the coals, it is necessary to view the proximate analysis on the pure coal (ash-, moisture-, and sulfur-free) basis. Either the fixed carbon as recalculated or the fuel ratios $\frac{\text{F.C.}}{\text{V.M.}}$ may be employed. In the following pages "fixed carbon" will be used to mean fixed carbon in "pure coal."

Appalachian Trough

The Appalachian trough presents probably the best region of the world for the observation of the progressive carbonization of the coals in

[6] D. White: The Effect of Oxygen in Coals. U. S. Geol. Surv. *Bull.* 382 (1909); Bur. of Mines *Bull.* 29 (1911).

passing from one side to the other of a great syncline. In the northern portion of the trough we find coals of the same formation and, in some cases, in identical or very nearly contemporaneous beds extending with

Fig. 1.—Regional progressive carbonization in the Northern Appalachian trough. Heavy black lines (isocarbs) "contour" the fixed carbon in ash- and moisture-free coal; thin dotted lines outline coal fields; rows of small crosses mark thrust fields.

but slight interruption from one side of the trough about 300 miles to the other side. On the western side, in Ohio, the fixed carbon of the Allegheny formation is between 55 and 60, with several small "islands" of

slightly greater or less volatile matter. Near the meridian of Pittsburgh the coals show fixed carbons of 60 per cent. Eastward the volatile matter falls off more rapidly and by the time Latrobe or Connellsville is reached, the coals are of coking rank with about 65 or 66 per cent. fixed carbon, while at Windber, or practically at the eastern margin of the Allegheny bituminous area, the fixed carbon approximates 83 per cent., the difference being about 20 per cent. in 70 miles. In the Broadtop field the fixed carbon is variable and hardly reaches the latter figure, though the basin is much farther to the eastward. We shall again refer to this field. Still farther eastward and bearing slightly to the north, the western end of the southern anthracite region shows a carbonization of barely anthracitic rank, while in the Lehigh area, farthest east, it approximates 97 per cent.; see Fig. 1.

Between Clarksburg, W. Va., and the Georges Creek basin near Cumberland, Md., the Pittsburgh bed gains 22 per cent. in fixed carbon, the distance being only 70 miles. The lower Kittanning coal gains nearly as much between the Allegheny River and the Allegheny escarpment in Cambria County, Pa., the loss of volatile matter being 20 per cent. in about the same distance.

A similar gradient is observed in passing from Ironton on the Ohio River to Quinnimont or Pocahontas (82 per cent.), or from the western outcrop of the Warrior coal field eastward to Birmingham, though the coals at the eastern margin of the latter field hardly reach the semibituminous rank (75 per cent.). As in the Broadtop field, the coals of the Coosa and Cahaba basins, to the east of the Warrior field, show fluctuating fixed carbons, the greatest of which are but little in excess of that at the eastern edge of the Warrior field.

Interior Paleozoic

The regional progressive carbonization of the coals toward the east in the Appalachian trough, toward the southeast in the broad, flat Illinois-Indiana basin, and toward the south and east in the Mid-Continent fields, is graphically shown by "contouring" of the fixed carbon in the map, which was compiled in small scale from state and regional carbonization maps by the writer in 1914.[7] The contours then drawn are subject to but slight revision in consequence of later coal-field exploration and, particularly, the extension of the areas covered by standardized

[7] D. White: Some Relations in Origin Between Coal and Petroleum. *Jnl.* Wash. Acad. Sci. (map) (1915) **5**, 189–212. This map was prepared especially to show the relation of the regional progressive carbonization of the coals to the general rank, as shown by gravity, of the oils in the same or underlying formations, and the extinction of commercial productivity of petroleum, except in insignificant amounts of white oils, in areas where the carbonization of the coals in the normal sequence exceeded a percentage approximating 63 to 66. This publication has long been out of print.

analyses made in the laboratories of the Bureau of Mines.[8] Larger scale mapping with contouring of the fixed carbon (isocarbs), based upon more voluminous data, have been published by D. B. Reger[9] for West Virginia, G. H. Ashley for Pennsylvania,[10] D. R. Semmes[11] for Alabama, and J. Brian Eby[12] for southwestern Virginia and adjoining portions of Kentucky, West Virginia and Tennessee. Regional carbonization in the Paleozoic area of northern Texas has been discussed and mapped by M. L. Fuller.[13]

Western Cretaceous and Tertiary

The Cretaceous and Tertiary coal basins of the Western States are generally much less extensive and deeper than those of the East, and in most cases the coals are of lower ranks. Nevertheless in many of the areas progressive carbonization is clearly shown in following the outcrops in the direction of greatest compression.

The coals of the Fort Union (lower Eocene), which are mined in the northern Great Plains and Rocky Mountain region are brown lignites in North Dakota, as at Wilton and Lehigh,[14] but when followed westward are found to be mainly black or extremely dark, but essentially lignite, in the longitude of Miles City and Glendive, Mont., while still farther west, near Red Lodge, they verge into the bituminous rank. The coals of the underlying Cretaceous advance in the same direction. The Fort Union coals are generally distinctly xyloid and are perhaps as uniform in their

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[8] For both approximate and ultimate analyses of coals from American coal fields see N. W. Lord: Analysis of Coals in the United States, with descriptions of mine and field samples collected between July 1, 1904 and June 30, 1910. Bur. of Mines *Bull.* 22 (1912); A. C. Fieldner, H. I. Smith, A. H. Fay and Samuel Sanford: Analyses of Mine and Car Samples of Coal Collected in the Fiscal Years 1911 to 1913. Bur. of Mines *Bull.* 85 (1914); A. C. Fieldner, H. I. Smith, J. W. Paul and Samuel Sanford: Analyses of Mine and Car Samples of Coal Collected in the Fiscal Years 1913 to 1916. Bur. of Mines *Bull.* 123 (1918); A. C. Fieldner, W. A. Selvig and J. W. Paul: Analyses of Mine and Car Samples of Coal Collected in the Fiscal Years 1916 to 1919. Bur. of Mines *Bull.* 193 (1922); Analyses of Kentucky Coals. Bur. of Mines *Tech. Paper* 308 (1922); G. S. Rice, A. C. Fieldner and F. D. Osgood. Analyses of Iowa Coals, Bur. of Mines *Tech. Paper* 269 (1921); Analyses of Ohio Coals. Bur. of Mines *Tech. Paper* 344 (1923); David White: The Effect of Oxygen in Coal. U. S. Geol. Surv. *Bull.* 382 (1909); M. R. Campbell: The Coal Fields of the United States, General introduction. U. S. Geol. Surv. *Prof. Paper* 100-A and J. A. Bownocker: The Coal Fields of Ohio. U. S. Geol. Surv. *Prof. Paper* 100-B.

[9] *Trans.* (1921) **65**, 522.

[10] G. H. Ashley and J. F. Robinson: Oil and Gas Fields of Pennsylvania. Penna. Geol. Surv. (1922) **1**.

[11] D. R. Semmes and J. E. Brantley: Ala. Geol. Surv. *Bull.* 22 (1920) 54.

[12] J. Brian Eby: Va. Geol. Surv. *Bull.* 24 (1923) Plate 37.

[13] M. L. Fuller: *Econ. Geol.* (1919) **14**, 536.

[14] A. G. Leonard and C. D. Smith: U. S. Geol. Surv. *Bull.* 341 (1909) 15, 36, 62; U. S. Geol. Surv. *Geol. Atlas*, Folio 181.

constitution as the Paleozoic coals of Illinois. Proof of horizontal pressures increasing to the westward is abundant.

In general, the carbonization of the Cretaceous and Tertiary coals in other regions of the Western States progresses toward the mountain uplifts, just as in the Montana-Dakota area. This is conspicuously the case in the Eocene coals of western Washington,[15] where the carbonization advances from a semilignitic rank of 45 per cent. fixed carbon in the Chehalis and Eufaula region through the subbituminous and low bituminous at Diamond and Ravensdale to coking rank at Carbonado and Wilkeson, while still farther to the east the coals near Fairfax and Montezuma, in the foothills of the Cascades, reach a carbonization of over 80 per cent. The coals higher as well as those lower in the same section change in the same direction, which shows that the differences are not due to floral distinctions, nor can they be caused by differences in climate or progress in initial decomposition. Similar eastward progression in carbonization is seen farther north, in Whatcom County, near the northwest border of the state, where, between Bellingham and Glacier, the carbonization steps from 66 per cent. fixed carbon to 92 per cent.

In the Glenwood Springs coal field of northwestern Colorado the upper Cretaceous coals outcrop practically continuously along the Grand Hogback from Newcastle and South Canyon on Grand River, through Diamond, Pocahontas, Sunlight and Gulch to Coal Basin.[16] At the north the fixed carbon of the coals falls below 56 per cent., but as the beds approach the Anthracite-Crested Butte uplift, the coals change to higher grade bituminous, with 60 per cent. fixed carbon at Sunlight; coking coal with well-developed cleavage and 62 per cent. fixed carbon at Gulch, and a highly prismatic coking coal with 75 per cent. fixed carbon at Coal Basin. On the opposite (south) side the same coal measures outcrop in the Book Cliffs field and along the Grand Mesa until it reaches the Anthracite-Crested Butte uplift from the southwest.[17] Here again, the coal beds become progressively devolatilized as they traverse the district of increased compression near the uplift.[18] Transition from bituminous through cooking rank to anthracite is also observed in passing from the southeast to Crested Butte and across to Floresta, where may be found anthracite indistinguishable by any criteria other than paleontological from some of the Pennsylvania anthracites. Tho Mesaverde coals of eastern Utah change from blocky, rather low bituminous to coking rank with pencil-prismatic structure at Sunnyside on the east.[19]

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[15] E. E. Smith: U. S. Geol. Survey *Bull.* 474 (1911).

[16] H. S. Gale: U. S. Geol. Survey *Bull.* 316 (1907) 264.

[17] W. T. Lee: U. S. Geol. Survey *Bull.* 341 (1909) 316.

[18] S. F. Emmons, C. W. Cross and G. H. Eldridge: U. S. Geol. Surv. *Geol. Atlas*, Folio 6 (1894).

[19] G. B. Richardson: U. S. Geol. Survey *Bull.* 371 (1909); Frank R. Clark: U. S. Geol. Survey *Bull.* (in press).

An exceptionally interesting example of regional progressive metamorphism of coals is found in the Trinidad-Raton district of southern Colorado and northeastern New Mexico. In passing along the outcrops of these coal measures from Strong and Pictou, southwestward toward Trinidad, the coals of the Vermejó and Raton series progress from a very low-rank bituminous, at the north, through successively higher ranks of carbonization into low coking quality in the region of Berwind and Hastings, and on to excellent coking rank, with about 67 per cent. of fixed carbon, at Starkville and Sopris or Engelville. In this field the carbonization advances from the flank of the Sangre de Cristo uplift southeastward toward the corner of the coal field, near Engelville; *i. e.*, away from the mountains.[20]

Alaska

In Alaska the coals of the Controller Bay field change from coking rank with about 77 per cent. fixed carbon to anthracite in passing from the northwest to the southeast, and in the Matanuska field they range from low-rank bituminous at the west to semi-anthracite or even to anthracite at the extreme east.[21]

Relations of Carbonization to Batholith Intrusions

It has been urged that the progressive carbonization noted above in Washington, Montana, and western Colorado, which takes place with steepest gradient as the mountains are approached, is due to the heat emanating from laccoliths, from batholiths, or from molten rock forced upward to form the cores, or along the axes of the ranges. An inspection of the geological maps of the coal fields shows that such rise of heated rock material in the process of mountain building can hardly account for the gradient in southwestern Washington, nor for that spreading from Anthracite to New Castle in Colorado, notwithstanding that the mountain on which Anthracite and Crested Butte are placed appears to be of laccolithic origin.

Western States

In northwestern New Mexico and southwestern Colorado the Cretaceous coals grade upward in passing from the south toward the mountains in the vicinity of Durango, where they approach semibituminous rank. However, the same coals, Cretaceous in age, not only grade downward in carbonization to the southeast and southwest, a circumstance which should not be overlooked by the driller for oil, but the fixed carbon is

[20] W. T. Lee: U. S. Geol. Surv. *Bull.* 752 (1924).

[21] A. H. Brooks: U. S. Geol. Surv. *Bull.* 259 (1906) 140; G. C. Martin: U. S. Geol. Surv. *Bull.* 289 (1906) 18; *Bull.* 327 (1907) 41; and *Bull.* 500 (1912) 75.

lower also to the westward as the coals approach the flank of the laccolithic Ute Mountains.

Most interesting relations between the direction of progressive carbonization, on the one hand, and the centers of intrusion on the other, are to be observed in the Trinidad field of Colorado. Here the coal advances in rank to the eastward—that is, in a direction away from the mountains—and the line of most rapid increase of fixed carbon may be at 60° to the axis of uplift. Meanwhile the coal measures pass from their upturn on the flank of the Dakota hogback to a nearly flat position along the eastern border of the field. Portions of the field are cut by dikes or sheeted by basalts so seriously as to impair the quality of the fuel as well as to deter its exploitation. But while the coal is altered or even coked in contact with the sills, the metamorphism is purely of the contact type and distinctly local.

Further, as shown in the Walsenburg and Spanish Peaks folios of the U. S. Geological Survey (Nos. 71 and 68), the group of great volcanic plugs forming the Spanish Peaks, from whose masses, several miles in diameter, the dominant system of intrusives radiates across the coal measures like sunbeams, lies in the northwestern part of the field. The fact that in passing from Trinidad northwestward to and around this center of igneous intrusion the volatile matter of the coals actually increases is most significant. Some of the coals of lowest carbonization yet reported in the basin lie at localities only a few miles from the great igneous stocks.

The theory of metamorphism by batholiths and igneous intrusives is more fully treated by the writer in his chapters on the origin of coal[22] and the results of contact metamorphism have been specially discussed in J. B. Eby's paper.[23] It is, however, worthy of note that in the Trinidad-Walsenburg field the coal appears to be virtually unaffected at a distance of more than a few feet from a thin dike. Generally there is little evidence of change either physically or chemically at a distance twice the thickness of the dike itself, even when the latter is comparatively small.

In the coal fields of western Washington the coal measures, generally horizontal at the west, become closely folded, faulted, overthrust, and crumpled in the foothills of the Coast Range. In this region the coals of low bituminous rank in the New Castle-Gillman area appear to be little, if any, affected by proximity to an igneous mass of truly mountainous proportions forming Squawk Mountain, but they are far more carbonized in the region of evidently greater compression farther to the east (Snoqualmie) and north (Cokedale). Willis reports that the coal nearest an eastward-lying eruptive mountain near Evans Creek has a

[22] Bur. of Mines *Bull.* 38 (1913) 101.

[23] Contact Metamorphism of Some Colorado Coals by Intrusives; see p. 246.

lower fixed carbon content than that somewhat farther from the igneous rock but stratigraphically lower. Apparently everywhere in this field the contact alteration of the coal is confined to a narrow zone not more than a few hundred feet from the largest dike. Thus, a thin coal bed that was converted to a brilliant anthracite near a dike more than a mile in thickness was seemingly wholly unaffected where again sampled less than a quarter of a mile from the dike.

In the Trinidad district of Colorado, although some of the highest rank coal of the region is found in the lower part of Great Mesa, which culminates in a basaltic flow about 700 ft. in thickness, known as Fishers Peak, the highest coal of the series—that is, that nearest to the great outflow—appears to be highest in volatile matter, the successively lower coals being higher in fixed carbon, in conformity with the law of Hilt.

The coal of the Cerillos field in New Mexico shows rapid increase of volatile matter where the wedge between it and the heavy sill above it thickens, while in the Controller Bay region of Alaska the highest carbonization is farthest from the dikes.

Eastern States

The volatile matter in the coals of the Southern Anthracite field, in Pennsylvania, increases through a distance of 65 miles to the southwestward, and is greatest at a point nearest to intrusives, probably of post-Triassic age, near Jonestown, about 10 miles to the southward. Still farther west, near the Susquehanna River, not far from Duncannon, the volatile matter is still greater in the Pocono (Mississippian) coals, which are, however, less than 5 miles from dikes. In the great bituminous region of the Appalachian trough the only known dikes are peridotites in Elliott County, Ky., in the region of nearly lowest carbonization at the western border of the field, and in Pennsylvania near Brownstown, which is west of the coking belt. The dikes near Ithaca and Syracuse, which are similar in composition and may belong to the same system of intrusives, are far to the west of the zone of anthracitization, near which no evidence of intrusives is known. In southern Illinois the dikes at Eldorado and Harrisburg are passed some distance before reaching the area of maximum carbonization to the southeast, though a volcanic plug has been found still farther to the southwest, where coals stratigraphically as low or lower are really higher in volatile matter.

The falling off in the fixed carbon of the coals in areas compensated by overthrust, and in particular the backward drop toward the margin of the overlapping strata, to which reference will later be made, is conclusively opposed to any theory that the carbonization of the coal in the direction of the axis of uplift is due to heat from deep-lying igneous rocks —batholiths or laccoliths.

Progressive Carbonization and Thrust Compression

Both the study of the regional geology and the examination of the microscopical constitution of the coals themselves leave no room for doubt that in most of the American coal fields the differential carbonization of the coals is primarily due to regional pressure-metamorphism. In the writer's chapters of the bulletin by Dr. R. Thiessen and himself on the origin of coal,[24] the evidence is reviewed more fully than is here possible, and the different theories are briefly discussed. It will suffice, accordingly, in this place briefly to note only some of the principal facts, particular attention being given to the compensating effects of folding and thrust faulting.

Carbonization Progresses toward Sources of Thrust

The increase of fixed carbon in the general direction of obviously greatest horizontal compression of the beds, so conspicuously evident in the Appalachian fields, is observed also in many Old World coal regions,[25] a circumstance which long ago led to the proposal of the horizontal pressure hypothesis. Failure of acceptance of the theory was, however, mainly due to the drops in carbonization and the variations in fixed carbon often found in strongly folded regions evidently nearer the sources of the pressure, and presumably subjected to greater stresses. Lack of increase in carbonization where still greater shortening of the crust plainly had taken place, was viewed as disproving the theory, and necessitating a different explanation such as (*a*) differences in the original composition of the plant substance in the coals of different carbonization; (*b*) different degrees of bituminization by hydrocarbons approaching from some outside source and impregnating the coals in different areas; (*c*) different temperature gradients, with consequently different degrees of distillation, resulting from igneous rocks occurring as batholiths, laccoliths, or intrusions; (*d*) differences in age; or (*e*) differences in biochemical bacteria.

Compensating Effects of Faults and Folds

On the other hand, as the writer has pointed out,[26] the areas of folding and faulting are areas in which the horizontal compressive stresses have been partially compensated and relieved by convolution and overlapping of the beds. Further, in every case this compensation took place before the maximum stresses were exerted. The strata in the Broadtop field and in the Cahaba and Coosa basins, for example, were never subjected to the final full power of the differential thrusts, which operated with

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[24] Origin of Coal. Bur. of Mines *Bull.* 38 (1913) 91–130.

[25] Bur. of Mines *Bull.* 38 (1913) 13; X. Stainer: *Ann. des Mines Belgique* [3] (1900) 5, 397, 529; W. A. I. M.; van W. van der Gracht: *Mem.* Gov. Inst. Geol. Expl. Netherlands (1900) 2, 113.

[26] Bur. of Mines *Bull.* 38 (1913) 114; *Jnl.* Wash. Acad. Sci. (1915) 15; *Trans.* (1921) 65, 176.

intermittently increasing stresses throughout long periods, with incredible compressive force,[27] and which in many regions were renewed perhaps at a different angle, at times of later diastrophic movement. The stresses ultimately exerted in these folded basins may have been actually greater, but preëxisting lines of weakness or lesser competency of the horizontal strata permitted yielding before the highest compression that otherwise would have taken place endwise of the beds was accomplished.

The Cahaba and Coosa basins in Alabama lie in wedges, each of which is not only folded somewhat, but actually shoved very obliquely upward to the westward over the edges of the strata in the region beyond, so that Cambrian rocks actually override Pennsylvanian. Therefore, the beds in these basins have actually endured less longitudinal compression, though overthrusting and folding have permitted greater shortening of the arc in this region of undoubtedly greater intensity of westward horizontal thrusting. There is no question as to the greater horizontal compression the beds would have endured had there been no buckling or faulting. It is therefore quite natural not only that the coals of the Cahaba basin should vary in volatile content according to the structure and the position of the sample with reference to the fold but also that at many if not all localities the coals should be less devolatilized than those within the eastern edge of the flat-bedded Warrior field, against which the blocks containing the Coosa basin are overthrust, and which resisted the transmitted stresses without yielding.

The Broadtop field in Pennsylvania lies in the midst of a folded region torn by notable thrusts (see Fig. 1), the full extent of which is not yet ascertained. Therefore, the strata of this field have never been submitted to the horizontal compression that would have been endured had the beds been held longer in a horizontal attitude by strata of greater competency acting in coördination with a more rigid basement through which the main forces were transmitted. The carbonization varies according to the mechanics of the structure, but it appears in no part of the field to be so high as it is near Windber, within the buttressed bituminous field 25 miles to the westward.

When, however, we pass around to the north of the great "valley region" of strong folding and faulting, in which the plication bows crescentically northwestward (see Fig. 1), we find the carbonization still advancing along beds essentially horizontal, until the coals approximate the anthracitic rank at Bernice. Still farther eastward, where the basin embracing the Northern Anthracite field is gently folded but not overthrust, the coal is of typical anthracite rank, with a fixed carbon of over 93 per cent. The highest carbonization of the anthracite region occurs, as might be expected, to the southeast in the direction of greatest thrust, where, in the Lehigh district, the fixed carbon reaches 97 per cent.

[27] *Op. cit.*, 13.

It is important to observe that in going from the Lehigh district—say Mauch Chunk—southwestward, along strike, the carbonization of the anthracite falls off as the coal basins extend out into the region of greater folding and faulting. This is well shown in the prongs of the Southern Anthracite field and of the Western Middle field.[28]

Fault Effects Confirm Explanation

More conclusive proof of the production of advanced dynamochemical changes (carbonization) by essentially horizontal thrusting of the beds is found in the reaction to buckling and to overthrust seen immediately behind the faults along the flank of or within the eastern margin of the bituminous coal fields themselves. If we follow the Allegheny front, the eastern border of the great Appalachian bituminous regions, around the arc of the above mentioned crescent and to the southwestward through southern Pennsylvania, Maryland, West Virginia, Virginia, and onward, it will be seen that in general the carbonization is highest where the beds in the zone bordering the coal field are less faulted and especially where less overthrust; but where the formations are overthrust at or near the border, the fixed carbon falls, the drop being greater where greater compensation of the thrust was given by farther over-riding of the beds. This feature is strikingly illustrated in several areas in which the stratigraphy and structure have been mapped in detail.

The fault which begins very close to Pocahontas, Va.,[29] originates rather abruptly in a low, narrow anticline which is quickly fractured, with increasing overthrust, without developing an arch of appreciable size, as it is followed southwestward parallel to the edge of the coal field. The compensation resulting from the thrust is immediately—in fact, instantaneously—observed in the declination of the fixed carbon of the coal for a short distance behind the fault, as shown in Figs. 1 and 2. The thrust grows in magnitude until near St. Paul, about 28 miles distant, Cambrian rocks lie on Carboniferous. Meanwhile the fixed carbon in the Pocahontas coal bed and in the overlying coals has rapidly declined from nearly 84 to about 65 per cent.

Passing a few miles northwestward from any point on the fracture, the fixed carbon is found to increase quickly to a maximum, beyond which it falls off in a gradient comparable to that of other regions in the corresponding zone of the basin. The maximum carbonization also falls off gradually as the overthrust gains in magnitude. At the same time, however, the individual isocarbs, or lines of equal carbonization, hook around to the east against the fault line. This is well shown in J. B.

[28] G. H. Ashley and J. F. Robinson: Penna. Geol. Surv. (1922) 1.

[29] M. R. Campbell: U. S. Geol. Surv. *Geol. Atlas*, Pocahontas Folio (No. 26, 1896) and Tazewell Folio (No. 44, 1898).

Eby's[30] detailed mapping of the progressive carbonization of this region, which through Mr. Eby's courtesy the writer reproduces as Fig. 2.

Pine Mountain, a long anticline parallel to and about 15 miles within the eastern border of the coal field, and forming the western border of the

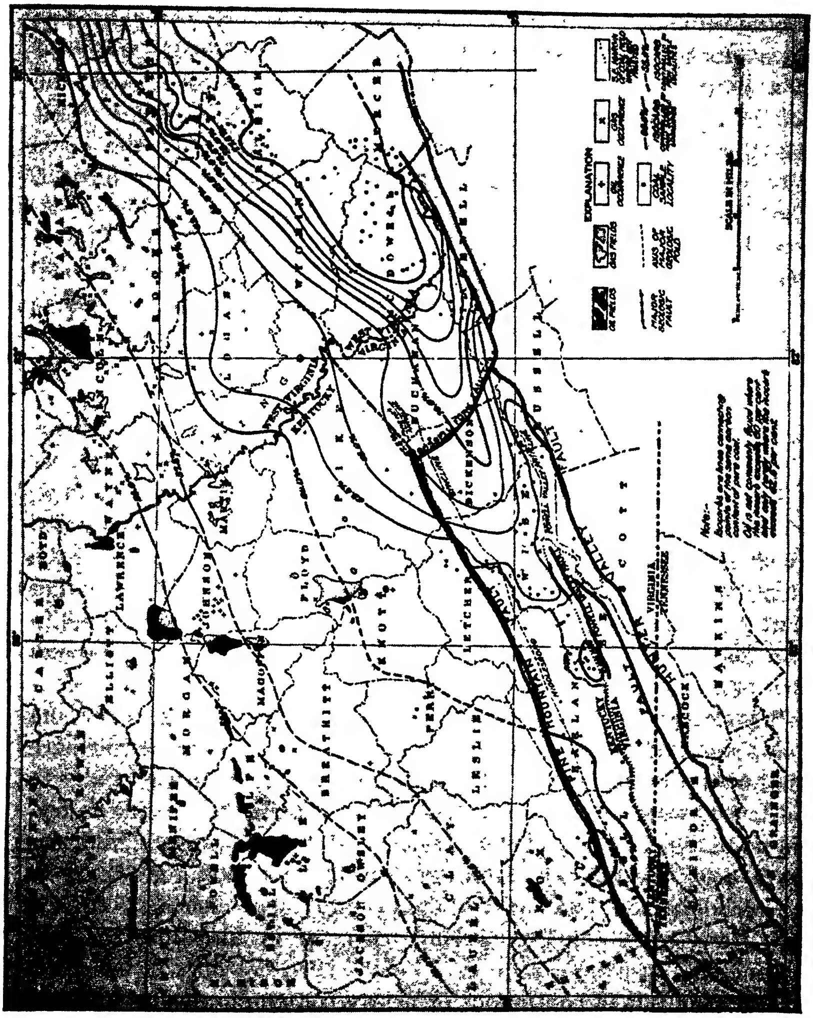

Fig. 2.—Regional progressive carbonization of Southeastern Virginia and adjacent portions of West Virginia, Kentucky, and Tennessee, as indicated by contours showing fixed carbon of the coals; by J. Brian Eby.

Cumberland coal basin, is an overthrust, rather sharply developed fold, the maximum displacement of which is sufficient to bring the Devonian black shale partially into view. As this fault develops in magnitude toward the southwest the carbonization rapidly declines to less than 62.5 per cent., and even below 60 per cent. before the fault dies out at the

[30] Va. Geol. Surv. *Bull.* 24 (1923) Plate 37.

intersection of the Elk Valley fault in northern Tennessee, beyond which point the carbonization again advances to 70 per cent. Just as the Elk Valley fault, last mentioned, marks an offset of the Pine Mountain fault to the southwest, so the Russell Fork fault in Buchanan and Dickenson Countries, Va., marks a shear zone offset at the northeastern end of the Pine Mountain fault. Thus, the Cumberland basin may be regarded as lying in a great block overthrust by older beds on the east, and itself shoved a short distance (increasing toward the southwest) across the edges of the flat-lying coal measures of the main coal field. As a result of these thrust-absorbing movements, the fixed carbon of the coals declines to about 60 per cent. throughout the southwestern two-thirds of the Cumberland basin, as shown in Eby's map, Fig. 2.

In crossing the Warrior coal field of Alabama the carbonization of the coals in the nearly horizontal strata advances from about 55 to 70 per cent. near Birmingham,[31] where the great wedge containing the Cahaba field is thrust to the northwestward so that Cambrian shales overlie coal measures of Pottsville age. Here, again, some hooking backward of isocarbs immediately behind the overthrust is to be noted, though the analytical material is not so ample as that in southwest Virginia. In both the Cahaba[32] field, which lies in the first great overthrust wedge east of the Warrior field, and the Coosa basin, next eastward, which also lies in an upward wedged block, the varying carbonization of the coals is in general scarcely more advanced than in those behind the edge of the Warrior field, as is to be expected. No coals are found farther east; but the very richly carbonaceous shales, of Mississippian age, in northern Clay County, Ala., are partially graphitized, apparently through no other cause than increased regional thrust pressure.

In the Eastern Interior basin which embraces the Illinois-Indiana coal field, slight fluctuations in carbonization are seen in the northern portion, but in the southern third the carbonization advances rapidly to the southeast, where it approximates 65 per cent. in the Saline valley. At this point buckling sets in, in evidence of thrust pressure from the southeast, and beyond here faulting accounts not only for failure in further carbonization but for variability and local decrease of fixed carbon. Here, as in the Cumberland basin, or in Alabama, the progressive increase in fixed carbon may be observed not only in beds in a single formation but in continuous or nearly contemporaneous deposits.

The coals of the Mid-Continent field advance from a very low bituminous rank in Iowa, northwestern Missouri, and northeastern Kansas,

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[31] Charles Butts: U. S. Geol. Surv. *Geol. Atlas*, Birmingham Folio (No. 175, 1910).

[32] Charles Butts: The Northern Part of the Cahaba Coal Field. U. S. Geol. Surv. *Bull.* 316 (1907) 76–115; The Southern Part of the Cahaba Coal Field. U. S. Geol. Surv. *Bull.* 431 (1911) 89–146; U. S. Geol. Surv. *Geol. Atlas*, Bessemer Vandiver Folio (in press); U. S. Geol. Surv. *Geol. Atlas*, Columbiana-Monteval Folio (in press).

to a carbonization of 60 per cent. in the vicinity of Muskogee, Okla. Southeastward in this region the coals grade upward through semibituminous to semianthracites, with fixed carbon in excess of 90 per cent. at the eastern end of the coal field, in Arkansas. Going westward along the southeastern border of this coal field, an overthrust zone known as the Choctaw fault is encountered. Behind this fault the carbonization of the coals rapidly declines as the fault increases in magnitude to the westward; also the isocarbs are conspicuously hooked backward as the fault is approached.

Stress is laid on the carbonization gradient behind the thrust faults as unmistakably indicating the immediate effect of relative escape from the maximum compressive stresses of the area, and as indirect but corroborative proof as to the effectiveness of horizontal compression in the progressive regional devolatilization of the coals. It not only shows clearly the effects of relief of the beds immediately behind the overlap from the full force of the compressive thrust, but it reflects variation in the intensity of the horizontal stresses, due mainly to the mechanics of the structure and thrust transmission.

Detailed studies based on more voluminous chemical analyses of the areas embracing several of the great thrusts, such as those at Pocahontas and Pine Mountain, and in the Birmingham district, will probably result in data from which approximately to deduce the lines of transmission of the thrust forces through the massive and relatively competent rocks beneath the folded or even contorted strata and the thrusted wedges, and through the undisturbed horizontal strata riding competent beds beyond the faults or folds. The rate of catching up of the fixed carbon to the maximum behind the Pocahontas, Pine Mountain, and Choctaw faults seems to show a low gradient of the plane of thrust transmission to the now exposed strata in these areas. The width of the zone of abnormal volatile matter (decline of carbonization) depends upon the depth of the faulting. It may be added that local variations in fixed carbon, probably not due to original differences in the constitution of the coals, may owe their origin to local differential stresses such as produce local and irregular anticlines and domes.

Carbonization Greatest in Areas Resisting Greatest Thrust Stresses

The greatest compression takes place on the side from which the thrust originates. From this point the force is gradually reduced (compensated) by actual compression of the rocks, if not by folding and faulting, so that the thrust is gradually weakened in passing farther and farther from its initial point. The general gradient in carbonization reflects the diminution of horizontal thrust. The compressibility of many of the sedimentary rocks is more or less well known to engineers, but is not fully realized

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by most geologists. Experiments showing the measurable compressibility of granites and other igneous and crystalline rocks have been described by F. D. Adams, and by L. H. Adams and others.[33]

Relative to the great horizontal stresses to which the strata in the Appalachian trough have been subjected, mention may be made of the calculations by several eminent geologists of the shortening of the crust of the earth in different portions of the northern Appalachian region. Claypole,[34] it will be remembered, roughly computed the contraction between the Allegheny front and Blue Mountain, 49 miles distant, at 9 miles; and that 95 miles had been contracted to 16 miles between Blue Mountain and the east side of Cumberland Valley. Lesley estimated the reduction by means of folding and faults at about 40 miles. More recently R. T. Chamberlin, an authority on tectonics, carefully calculated the shortening produced by folding alone of the Paleozoic rocks between Tyrone, Pa., and Marysville, Pa., 61.6 miles distant, at 10.2 miles. This estimate does not take into account the shortening effected by thrust faulting. Chamberlin also concludes that 9.5 miles have been reduced to 4.75 between Marysville Bridge and Harrisburg. More recently Arthur Keith,[35] than whom no geologist is more competent in knowledge of the stratigraphy and structure of the Appalachian region, has estimated the shortening that has taken place between tidewater on the east coast and the west side of the Appalachian trough at over 200 miles.

Pressure, Temperature and Time

The same metamorphic agencies that cause the devolatilization of the coals produce corresponding changes in the accompanying rocks, though these changes are not so marked until the later stages are reached. Dehydration of silts, compacting, progressive jointing and induration of sandstones, limestones, and shales, with, later, the development of platy cleavage and schistosity, with recrystallization of limestones, silicification of sands to quartzites, transformation of shales to slates, and deformation of grains or pebbles, take place while the peats are being progressively robbed of their moisture and reduced in volume by compression, and by loss of volatile matter in the form of gases, some of which probably condense in other strata, and while, in some cases, schistosity of the coal is apparently followed by cementation. In short, the regions of greater change in the coal show physical evidence of greater pressure.

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[33] Frank D. Adams and E. G. Coker: An Investigation into the Elastic Constants of Rocks, More Especially with Reference to Cubic Compressibility. Carnegie Inst. Wash. *Pub.* 46 (1906); Leason H. Adams, Erskine D. Williamson and John Johnston: The Determination of the Compressibility of Solids at High Pressures. *Jnl.* Amer. Chem. Soc. (1919) **41**, 1–42; Leason H. Adams and Erskine D. Williamson: On the Compressibility of Minerals and Rocks at High Pressures. *Jnl.* Franklin Inst. (1923) **195**, 475–530.

[34] E. W. Claypole: *Amer. Naturalist* (1885) **19**, 257.

[35] Arthur Keith: *Bull.* Goel. Soc. Amer. (1923) **34**, 335.

Devolatilization of coal is still in progress in many parts of the world; in some districts the rate is almost insensible; in others it is not only clearly perceptible, but obvious.[36] There is no line of demarcation between the different ranks of coal, the intergradation or continuity being absolute and complete between peat, lignite, and semigraphitic coal.

The transformation of the fuel from the peat stage, or primary rank of coal, to the more advanced ranks, as it is grossly indicated by the progressive reduction of the volatile matter in the fuel, is the product of the dynamochemical process.

The effective pressures are essentially those of horizontal thrusting exerted in tremendous but varying force intermittently through long intervals, especially during periods of diastrophic movement. Generation of volatile matter, including gases, in the beds, furnishes additional pressure. Pressure of loading assists in reduction of volume, mainly by dehydration, but its most important function lies in its aid to competency.

The temperatures of coal alteration even, to the anthracite ranks, have almost certainly been relatively low. They are the results of heat of depth of burial, heat of chemical reaction, and, what is far more important, heat of friction under the compressing stresses. The intermittent thrusts of generally increasing violence, exerted through long periods, with consequent actual horizontal compression of the rocks, can only have resulted in very great friction, the heat of which should be more or less cumulative. Observations by C. E. Van Orstrand of temperatures in deep wells on several anticlines in the United States indicate steeper temperature gradients as the axis is approached. This, however, is perhaps wholly explained by the greater rapidity of erosion of the rock material from the top of the uplift as compared with the rate of radiation of the heat.

The time during which the rock pressures have been exerted is geologic, and the pressure temperatures have probably been relatively low. It is important to note that essentially the same chemical results, so far as they are revealed by present methods of analysis, have been produced by greater intensity of thrust exerted through shorter periods, as by relative mildness of dynamic activity through a long period. This is well illustrated by the rapid advance of Cretaceous and Eocene coals to the coking and even anthracitic ranks in some of our western coal fields where, by forced marches, so to speak, the young coals have been brought to a stage of evolution as far advanced as the Paleozoic coals of western Pennsylvania or southern West Virginia. The accomplishment of relatively great alteration during a relatively short time premises more vigorous compressive stresses. In other words, the extent of the alteration of the coal depends on the duration as well as the intensity of the

[36] A striking illustration of copious escape of volatile matter is seen at the Coryell mine, near New Castle, Colo.

stresses. In the Paleozoic coal fields regional thrust compression has in some cases been accomplished during several periods. The eastern portion of the Appalachian trough not only was subjected to severe westward thrusting, with consequent buckling during the post-Paleozoic revolution, but the arc was further shortened at the time of post-Triassic compression. Further stresses were presumably exerted at the times of post-Cretaceous and post-Tertiary uplifting.

Bearing in mind that folding and faulting tend to compensate and neutralize the thrust stresses and that the degree of devolatilization of the coal depends in general on the duration as well as on the intensity of the compression, it becomes obvious that in regions of initial equal stress the metamorphism will, other things being equal, be greater in the districts where no buckling or overthrusting of the beds has permitted escape from the intensity of the thrust. The coal of the folded and especially the faulted areas may be less devolatilized than coal in other areas in which pressures, actually less intense, have continued for a longer period without relief.

Time and temperature may, within limits, each be substituted for the other, in accordance with field geological observation and laboratory experiment, and pressure is partially interchangeable with both.

The fact that under the same dynamic conditions coals of all ages —Paleozoic, Triassic, Cretaceous, and Tertiary—are brought to the same states or ranks, is proof that the ranks of the coal are not dependent on climate, ingredient matter, bacteria, or progress of initial decomposition. The fact that all the coals in the vertical sections are simultaneously advanced in passing into regions of greater sustained compression, regardless of type or ingredient material, shows that the geochemical changes are produced by a common dynamic cause.

Metamorphism of the Organic Matter from Rank to Rank

In the lower ranks of coal the principal chemical differences between coals of different types, but of the same rank, are due, as has been pointed out, to distinctive qualities inherited from the corresponding peats, they being due to the original ingredient constituents. At later stages, in higher ranks, the original distinctions yield to the effects of dynamochemical transformation, and become less conspicuous, while new qualities such as that which causes caking, originate in the course of the evolution of the coal.

Inherited Qualities

The relations between the chemical composition of the ingredient organic debris composing the deposit, on the one hand, and the peat aggregate, the lignite, and the subbituminous derivatives, on the other,

are illustrated in the accompanying table,[37] which roughly shows also some changes in chemical composition, so far as the latter are indicated by the ultimate analysis, as the coals advance to higher ranks.

In this table are given analyses representative of the principal types of fossil fuel deposits, each in the successive major ranks or stages of its evolution. The types are (1) the more or less distinctly woody or common ("humic") coals, (2) the canneloid types, (3) the ordinary sapropelic or bituminous shale, and (4) the algal sapropel or boghead coal. At the top of the same table are shown also the gross chemical composition of some of the most important of the somewhat resistant plant substances and products originally contributed to the organic deposit.

The directness with which each type of coal as seen in the different ranks reflects chemical qualities inherited from the plant structures and products surviving the biochemical process and characterizing the type of deposit in the peat stage is shown still more distinctly in the graphic curves of Fig. 3.

These curves are subject to revision when ultimate analyses of typical pure algal bogheads in the lignitic and subbituminous ranks are available, and they may be elaborated in details of very great interest when the analytical data obtained from coal samples systematically collected by the geologist in the field are so complete that, instead of quoting a single composite analysis as representing the average composition of coals of the particular type within the range of a given rank, it may be possible to submit a sequence of ultimate analyses illustrating the evolution of the type throughout the successive stages of that rank. Standard analyses of lignites grading from Pleistocene peats to the high-rank brown coals of Texas and North Dakota are especially needed. With such information, we should know at what point in the transformation of a given type of deposit the chemical changes marked by notable eliminations of carbon, hydrogen or oxygen occurred, with consequent effects upon the gross proportional relations of the other two principal ingredient elements. Such a series of analyses should also offer a better basis for speculation as to the hydrocarbons generated, including both those that remain in the solid residue and those that pass off as volatile matter.

The effect of the carbohydrates, which predominate in the initial sediments forming the common (humic) coals, is seen in the high oxygen and the relative low hydrogen[38] and carbon contents of those coals, as is clearly shown by the curves. The large content of hydrogen in the resins, the waxes, and the waxy-fatty elements of the spore and pollen

[37] From manuscript of "Some Relations between the Composition of Coals of Different Ranks and the Composition of the Initial Sedimentary Deposits," contributed to the semi-centennial meeting of the Société Géologique de Belgique, June, 1924.

[38] The vertical scale of the hydrogen curve is double that of the oxygen and carbon curves.

TABLE 1.—*Analyses of Humic Coals and Sapropelic Deposits*
(Ash, moisture and sulfur free)

	Humic Series					Sapropelic Series				
	Specimen	C	H	O	N	C	H	O	N	Specimen
Raw materials	Carbohydrate[1]	40.0–51.7	5.8–6.3	42.9–49.68		76.8–85.7	9.7–12.9	0 –12.12		Resinic matters[8]
	Average 24 woods[2]	49.31	6.69	44.4 (+N)		80.3–81.6	13.1–14.1	4.5– 6.6		Waxes[6]
	Straw[3]	48.27	6.36	44.75		74.0–78.	10.2–13.4	9.4–15.7		Fats and oils[6]
	Starch[4]	44.44	5.88	49.68						
	Wood + 10% average resins[5]	53.98	6.94	39.08		79.80	10.78	9.42		Copal, Madagascar[7]
						48.61	7.88	38.53 (+S)	4.98	Sapropel, calcareous[9]
	Humic acid	65.31	3.85	30.83		53.07	6.69	34.61 (+S)	5.63	Average of 6 sapropels[1]
Peat stage	Average 10 peats[11]	60.53	5.56	33.81		63.64	6.91	29.66		"Mature" peat[14]
	Briesen brown peat[12]	51.34	6.54	37.79 (+S)	4.33	79.4	12.0	8.9	0.7	Coorongite[15]
	Dopplerite[13]	56.46	5.48	38.06		77.65	11.33	11.12		Coorongite[16]
						73.8	11.0	13.5	0.6	Balkhash Lake[17]
Lignite	Average 22 Texas lignites[18]	69.82	4.72	25.46		64.06	10.03	24.70 (+S)	1.21	Miocene, Randecker Maar[19]
						65.16	8.51	23.99 (+S)	2.34	Miocene, Darmstadt[20]
						70.04	8.13	19.43		Debeque, Colo.[21]
						71.43	5.11	21.17		Lester, Ark.[22]
Sub-bituminous	Average 210 Mont., Wyo. Colo. and N. M.[23]	73.31	5.09	18.43	1.41	75.01	7.92	14.00		Cedar City cannel[24]
						71.28	10.12	17.51 (+S)	1.08	Oberkirchen[25]
Bituminous	Average 40 Ohio, Ind., Ill., Ia., and Mo.[26]	82.91	5.70	9.90		83.56	7.56	7.59		Leslie, Ky., cannel[27]
						85.97	10.81	3.22		Australian boghead[28]
						87.57	10.88	4.45		Scotch boghead[29]
						83.84	10.89	5.27		Tasmanite[30]
Semi-bituminous	Average 125 Raleigh and Fayette Co.s., W. Va.[31]	89.08	4.98	3.32	1.57					
Anthracite	Average 6 Penna. anthracites[32]	93.73	2.01	2.22	0.84					
Graphitic	Graphitic coal, R. I.[33]	94.10	0.69	4.81	0.25					
	Anthraxolite[34]	97.72	0.54	1.74						

[1] R. Thiessen: U. S. Bur. Mines *Bull.* 38 (1913) 291.

[2] F. W. Clarke: U. S. Geol. Sur. *Bull.* 695 (1920) 747.

[3] R. Thiessen: *loc. cit.*, 291.

[4] R. Thiessen: *loc. cit.*, 291.

[5] Theoretical composition average wood, plus 10 per cent. resinous materials. R. Thiessen: *loc. cit.*, 293.

[6] Average for coniferous resinoles and resinolic acids. R. Thiessen: *loc. cit.*, 293. For additional analyses of resins, see A. Tschirch: "Die Harze und die Harzebehälter," 1906; and F. Späte: "Die Bituminierung," 68, 1907.

[7] F. Späte: *loc. cit.*, 68.

[8] D. White: *Econ. Geol.* (1908) **3**, 310.

[9] From Belitshof near Berlin. F. Späte: *loc. cit.*, 46.

[10] Recent sapropels from Germany; sulfur included with oxygen. F. Späte: *loc. cit.*, 42.

[11] From northern United States. U. S. Bur. Mines *Bull.* 38 (1913) 292.

[12] Saprocoll near Briesen, West Prussia. F. Späte: *loc. cit.*, 66.

[13] Composite by Muhlberg. F. G. Kaufmann: *Jahrb. K-k.* Geol. Reichanst. (1865) **15**, 283; F. W. Clarke: U. S. Geol. Sur. *Bull.* 695 (1920) 753.

[14] Evidently sapropel. F. W. Clarke: *loc. cit.*, 750.

[15] From South Australia. Unpublished analyses by U. S. Bur. Mines.

[16] Engler, in "Das Erdöl," 269. Ed. by H. Hoefer. 4th ed., 1922.

[17] Turkestan. H. Hoefer: "Das Erdöl," 263. 4th ed., 1922.

[18] F. W. Clarke: *loc. cit.*, 756.

[19] Brown to whitish calcareous paper coal (Dysodilkalk) in the Miocene of the Randecker Maar, Germany: F. Späte: *loc. cit.*, 46.

[20] Sapropelic clay from the Miocene near Darmstadt in Germany. F. Späte: *loc. cit.*, 46.

[21] Rich oil shale from the Green River formation. Contains a little over 1 per cent. nitrogen: D. E. Winchester: U. S. Geol. Sur. *Bull.* 729 (1923) 16.

[22] Brown lignite about 5 ft. thick containing elongated lens of high-grade cannel, 2½ ft. thick. Sample includes the xyloid or normal lignite as well as the inclosed cannel, and therefore does not represent the hydrogen and oxygen values of the cannel. U. S. Bur. Mines *Bull.* 22 (1913) 49; see D. White: U. S. Bur. Mines *Bull.* 38 (1914) 15–19 and 48.

[23] Composite of analyses made in U. S. Geol. Survey and U. S. Bur. Mines. U. S. Bur. Mines *Bull.* 22 (1913) and *Bull.* 85 (1914).

[24] From the Colorado group of the Upper Cretaceous at Cedar City, Iron Co., Utah: D. White: *loc. cit.*, and G. B. Richardson: U. S. Geol. Sur. *Bull.* 341 (1909) 393.

[25] Bituminous dark coaly shale from the lower Wealdon at Oberkirchen in Schaumberg-Lippe, Germany (sulfur included with oxygen): F. Späte: *loc. cit.*, 47.

[26] F. W. Clarke: *loc. cit.*, 760.

[27] Contains a few preserved algae, though most of the material is spore exines with some cuticles and resins. D. White: *loc. cit.*, 44, 48.

[28] Alga coal (boghead), "kerosene shale," from New South Wales. B. Renault: "Microorganismes des Combustibles Fossiles," 155–156. 1893; see also F. Späte, *loc. cit.*, 87.

[29] Rich Scotch alga coal. B. Renault: *loc. cit.*, 166; F. Späte: *loc. cit.*, 67.

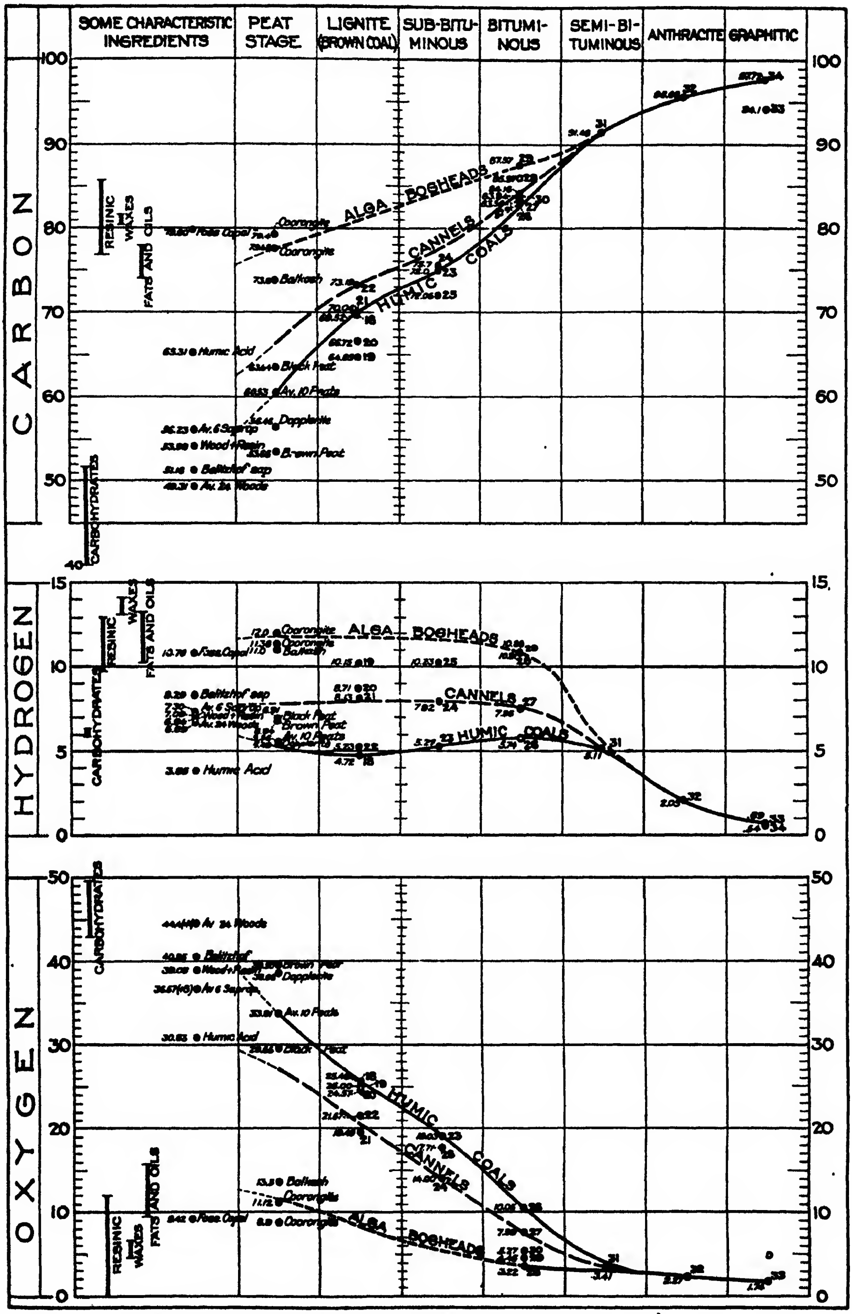
[30] A deposit made up almost entirely of exines of a single megaspore. F. Späte: *loc. cit.*, 68; and E. C. Jeffrey: *Jnl.* Geol. (1915) **23**, 220.

[31] Analyses made in U. S. Geol. Survey and U. S. Bur. Mines. These coals range from 75 to 83 per cent. fixed carbon in pure coal (ash, moisture, and sulfur free). See U. S. Bur. Mines *Bull.* 22 (1913) and *Bull.* 85 (1914).

[32] U. S. Bur. Mines *Bull.* 22 (1913) and *Bull.* 85 (1914).

[33] Average of 9 samples analysed by U. S. Bur. Mines and U. S. Geol. Survey. These analyses vary considerably in determinations of oxygen, which contains the residual error.

[34] From a coaly deposit in the Cambrian, near Sudbury, Canada. W. H. Ellis: *Chem. News* (1897) **76**, 186; A. P. Coleman: 6th *Ann. Rept.*, Ont. Bur. Mines (1897); F. W. Clarke: *loc. cit.*, 762.



CARBON, HYDROGEN, AND OXYGEN IN NORMAL (HUMIC) COALS AND IN ALGA (SAPROPELIC) COALS

FIG. 3.

exines, and the cuticular secretions, which predominate in and characterize the cannel type, is clearly reflected in the cannel curves, which also emphasize the lesser oxygen and the higher carbon contents as compared to the ordinary coals. The curves also indicate the calorifically richer volatile matter which is in much greater volume in the canneloid than in the humic type.

It will be observed that if the curves representing the carbon, hydrogen, and oxygen, in the humic, or woody, coals be protracted backward into the column showing the raw ingredient materials, they point directly to the carbohydrates as the principal mother substance from which these coals are derived. In fact, the curves for this type suggest a source in or near a mixture of woody matter with 10 per cent. of resins. That the canneloid curves do not flow more directly from the resin-wax percentages is probably due to the influence of the humic colloidal solution, now the ground mass, which is largely derived from the decomposition of carbohydrates.

On the other hand, the alga sapropels, Coorongite, and the algal coals, or bogheads, to the formation of which little terrestrial organic matter has been contributed, are conspicuous for their exceedingly high hydrogen, very high carbon, and remarkably low oxygen contents. In fact, the percentages of hydrogen, carbon, and oxygen in these richly "bituminous," ultra high-volatile deposits, correspond, at the initial stages, so closely to the percentages in average analyses of the waxes, fats, resins, and oils, that little room is left for doubt as to the leading part played by substances in or closely related to this group in determining the ultimate chemical composition of this type of deposit. From this similarity in gross chemical composition it appears probable that the microscopical, one-celled algae of the boghead are largely composed of waxy, fatty, or fatty-waxy matter.

Initial Characteristics Eliminated by Pressure-metamorphism

The changes in the relative proportions of the total carbon, the hydrogen, and the oxygen in the different types of deposits, as each is altered from rank to rank in passing from the peat or sapropelic stage to the anthracitic, are also very rudely indicated by the curves. These changes have been technically discussed by the chemists in the accompanying papers.[39] An important feature of them that is, however, superficially but tangibly shown by the curves is the well-known progressive loss of volatile matter, which roughly indicates the stage reached in the evolution of the type. The effects of the elimination of this volatile matter, generated under the influence of geologic processes, are apparent even at the outset. The rapid decline of the oxygen curve, the steep ascent of the carbon, and the general horizontality of the hydrogen curve, as the fuels progress from the peat stage through the ranges of the lignitic and

[39] Other preceding papers in this volume.

subbituminous ranks, are the conspicuous indices of the elimination of oxygen, which, in fact, expresses the general evolution of the coal more truthfully than does the conventionally determined fixed carbon.

The losses of hydrogen are relatively low, and while the amount of "available" hydrogen is gaining, there is no evidence of increase or enrichment of hydrogen in the process of bituminization. Hydrogen as well as oxygen is sacrificed in the losses sustained before passing beyond the top of the bituminous ranks, while the gross chemical distinctions between the types, including the inherited characteristics, rapidly become less evident.

With the loss of volatile matter in the higher bituminous and the semibituminous ranks, even the chemical distinctions shown by the ultimate analyses of humic coal, cannel, and boghead are rapidly wiped out, so that in the ranks marked by over 80 per cent. of fixed carbon, pure coal basis, the ultimate chemical analysis generally shows little if any difference between the algal, the canneloid, and the woody types. Progressive carbonization now appears to be the dominant feature of the changes, and in the anthracite ranks the analysis shows no distinction between the types, all the differences except the physical having disappeared. Apparently the ultimate stages of the organic deposits of the common coal type—namely, graphitic coal, graphites, graphitic shales, etc.—are indistinguishable by ultimate chemical analysis from the final stages of the sapropelic and algal types, the so-called "bituminous" deposits as they are represented in carbonaceous or graphitic argillites, slates, marble, and schists. As has been shown, the microscopical study of anthracites proves beyond question that the kinds of plant debris and plant products forming them, the conditions of their deposition, the variations in the progress of biochemical decomposition, and the differentiation of the humic, the cannel, and the sapropelic type have been the same as in the peat, the lignite, the bituminous, and other intermediate ranks.

Evolution by Carbonization (Bituminization)

The hydrocarbons now in the coals, as well as those eliminated in migrant gaseous or liquid states, were generated in the organic deposit itself in the course of its initial biochemical and its subsequent dynamochemical changes. "Bituminization" of the organic matter is produced in the course of the reduction of the ingredient material by biochemical action and the progressive generation under geological influences of volatile products, all of which are sooner or later eliminated.

Economically the most important feature of the evolution of coal is the deoxygenation of the deposit.[40] The elimination of the oxygen is essential to the progressive carbonization ("coalification") of the organic

[40] D. White: Effects of Oxygen in Coals. U. S. Geol. Surv. *Bull.* 382 (1909); Bur. of Mines *Bull.* 29 (1913).

deposit, including the humic colloidal derivatives and the secondary hydrocarbon products. "Carbonization" characterizes the progressive changes undergone by the preserved organic matter and biochemical decomposition products between the death of the plant or animal and the stage of essentially complete reduction to residual carbon, *in situ*. It marks the progressive evolution, which is, in effect, the metamorphism of the deposits.

Corrections for Contouring Fixed Carbon

In calculating and especially in illustrating progressive regional carbonization by "contouring" (isocarbs) two sources of error are particularly to be regarded: (1) the local error that may be caused by the use of an analysis of a very fatty, or high volatile, coal such as cannel, or a coal in which the fatty residues are concentrated by advance of the biochemical process. Attention must therefore be given to the physical as well as the chemical characteristics of the fuel. However, even when analyses only are in hand for inspection, the fatty nature of the coal can generally be detected by its distinctly low moisture, the confirmatively high available hydrogen, and the consequently rather high calorific value of the pure coal, and finally by the usually high ash. (2) The generally progressive downward increase in carbonization in any normal vertical section in accordance with the law of Hilt must be taken into account to secure greatest accuracy of representation. In working out the application of this law, discriminative attention must again be paid to variation in the ingredient constituents of the coals, such as the dominance of spore elements or fusain in the deposits. In another paper[41] the writer has discussed the law of Hilt more fully, with citations of examples illustrating the apparent rate of downward increase in fixed carbon within the first 3000 ft. in different areas. Data are not yet available for a satisfactory approximation of these rates, which seem to vary widely in different fields, with coals of different ranks and under different structural conditions.

The thorough study of the law of Hilt opens some very fascinating and profitable problems that invite the attention of the stratigrapher well grounded in geophysics. It may be remarked in passing that while the downward increase in carbonization is doubtless affected to some extent by greater depth-heat of the deeper beds, the change is probably due mainly to lateral pressures under loading or cover by rigid formations. In the process of carbonization the function of the overlying rocks is largely to hold the carbonaceous sediments in place—*i.e.*, the function of giving competency—rather than that of mere downward pressure of weight. Certainly the rate of downward increase in fixed carbon can be due only in part to rate of increase in the thickness of the overload, as has been assumed by some geologists.

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[41] Bur. of Mines *Bull.* 38 (1913) 25.

DISCUSSION

A. C. Fieldner, Pittsburgh, Pa.—It is of great importance that chemists should trace the chemical changes that have taken place in the constituents of coal during the alterations in progressive carbonization. Most chemists have worked upon isolated collections that happened to be in their particular neighborhood without much consideration of the regional change in this coal bed due to geological influences, nor have they kept in view the succession of ranks of coal, beginning with brown coal as a member of the lowest rank and ending with anthracite as a member of the highest rank in the coal series. Students of the origin and constitution of coal, in America, have had the opportunity of observing practically all stages in the rank variation of coal, inasmuch as almost every variety of coal is represented in North America.

Homer G. Turner, Bethlehem, Pa. (written discussion).—One of the remarkable things about science is the way old theories cling to life in spite of overwhelming evidence against them. They weaken slowly and gradually until some scientist ends their struggle with a blow so forceful that they leave the world of truth; credited no longer except by a few individuals with whom they hold spiritualistic communications through the operation of that type of mentality possessed by those who still think the world is flat. In this paper, the author strikes what should be a death blow to the theory that the various ranks of coal are due to original differences.

The results of dynamochemical changes, as deduced from a study of many coals of various ages and from different fields, are very convincing. The apparent anomalies have been squarely met and conclusively explained. It is of interest to note, also, that the theory of dynamometamorphism holds true in spite of effects of faults and of igneous intrusion.

The charts showing the original composition of ingredient organic debris and the progressive changes in the various ranks and types of coal give a wealth of information in a concise and understandable form.

The theory of progressive regional carbonization of coals is finally confirmed by those who have made a study of the microscopical characteristics of coals. My own observations in connection with anthracite show that woody bituminous coal and anthracite of the same type exhibit no essential difference in ingredient material when viewed under the microscope.

W. A. I. M. van Waterschoot van der Gracht, Ponca City, Okla. (written discussion).—The author gives an excellent synopsis of what we so far know of regional metamorphism affecting coals (and also other hydrocarbons). The fossil fuels are much more sensitive indicators of metamorphism than other rocks and hence are of special value for the

valuation of compressive forces that have affected certain regions, without having become of a magnitude that other rocks have been visibly altered or even schistose cleavage has been developed.

The author mentions, but I would like to emphasize especially the fact that tectonic carbonization need not be regarded exclusively in the light of the principal visible diastrophism that has deformed the sequence in which the coals are intercalated. The Permo-Carboniferous diastrophism is the main visible deformation of the Carboniferous Coal Measures, as the Andine diastrophism is that which has affected the Mesozoic coals of the West. Pressure, however, did by no means end then.

The great continental masses of the world have been folded in successive phases around the very old primary shields that form the nuclei of most of them. Such folded regions thereby apparently acquired a comparatively greater rigidity and withstood better subsequent pressure of later diastrophic phases. These later phases, however, clearly also affected them, only differently and not causing a second deformation of the same nature, except in rarer cases. Subsequent major diastrophisms evidently affected the whole continental mass; but the deformation was on a broad scale: the superficial expression of broad folds in the more plastic deep basements, and breakage in the more rigid upper crust; faults, broad uplifts and depressions, and gentle undulations in the blanket eventually present more recent deposits of later epicontinental seas. Thus the Appalachians in their present topographic expression, the Cincinnati Arch, the Ozarks, etc. are clearly caused by deep-seated basal deformation of the continental mass ("plis de fond" of the modern Swiss geologists) in late Mesozoic-Tertiary time, contemporaneous with the diastrophism in the Tethys and along the western Pacific margin of the American continent. One of the best proofs of such movements is the tilting of Mesozoic and Tertiary peneplains.

These later forces, which deformed the rigid continental mass, often entirely irrespective of the older trends of folding, must have been very severe, and may very probably have added considerably to the carbonization of the coals, especially because these are stresses that have found but little relief in the rigid masses.

A. C. Noé, Chicago, Ill. (written discussion).—Besides having a peculiar scientific interest for the coal geologist, this paper touches on a subject of vital importance to any petroleum geologist whose work is in the Pennsylvanian. There is a relation of the regional progressive carbonization of the coals to the general rank, as shown by gravity of the oils in adjacent formations. This aspect of Doctor White's problem has been treated by him in a paper published in 1915, which has long been out of print. The present paper gives new access to many facts bearing on this relation and is therefore highly welcome for this reason alone, besides being of immense purely scientific interest.

Moisture as a Component of the Volatile Matter of Coal*

By W. T. Thom, Jr.,† Washington, D. C.

(New York Meeting, February, 1925)

In previous classifications of coal, it has been customary to regard moisture eliminated from coal samples between 20° and 100° C. as extraneous matter, rather than as a constituent part of the coal. It seems, however, that the physical character and use properties of the low-rank coals are directly related to the amount of such moisture present, and recent chemical work has shown[1] that such coals contain unstable groupings which decompose between 20° C. and temperatures somewhat above 100° C., with the splitting off of moisture. According to this view, the moisture eliminated from air-dried coal below boiling point is similar in all essential respects to moisture eliminated above 100° C., and is produced by analogous reactions; and inasmuch as the moisture given off above 100° C. has always been treated as a constituent of the volatile matter of coal, it would seem that consistent usage would include as a part of the volatile matter all moisture present as an essential component of the coal as it occurs in nature. As a matter of experience, it seems clear that the general physical and chemical characteristics of the low-rank coals are largely determined by or related to the moisture, whether chemically or physically combined, present in air-dried coal; it is also demonstrable by trial that the low-rank coals cannot be satisfactorily classified on a purely chemical basis by using the moisture free form of analysis.

The low-rank coals of the western United States include numerous well-defined types, many of which were referred to in a classification proposed by Ashley,[2] in which the physical and use properties of the coals were made the primary basis for their systematic grouping. When testing this classification by replotting analyses of these type coals according to the Seyler scheme of classification,[3] a satisfactory parallelism between use properties and chemical constitution of the dry coal was found among

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[1] E. T. Erickson: Personal communication.

[2] G. H. Ashley: A Use Classification of Coal. *Trans.* (1920) **63**, 782.

[3] C. A. Seyler: Analyses of British Coals. *Coll. Guard.*, (1924) 41.

the high-rank, low-moisture coals, but an overlapping of types was evident in the lower rank coals. A similar overlapping of the low-rank coal types is evident when representative analyses are plotted according to a system similar to that proposed by Parr.[4]

Because it had been impossible to effect a practicable classification of the lower rank coals on a chemical basis by using the moisture free form of analysis, physical as well as chemical criteria for classification were set up by the U. S. Geological Survey,[5] for the separation of lignite and subbituminous coals from each other, and from the lower rank bituminous coals. Such a system is, however, subject to objection because it consists essentially of a classification according to personal judgment and experience, and involves decisions into which the personal equation enters largely.

In seeking to overcome this difficulty, the writer plotted about 800 analyses of composite samples of representative American coals according to a system suggested by Miss Taisia Stadnichenko, as a result of the work of a former student of Professor Parr's, with, however, the modification that the moisture of the air-dried form of analysis was considered as part of and was added to the volatile matter reported in the proximate analysis. Thus, by calculating the air-dried form of the proximate analysis to an ash-free basis, and by plotting volatile matter plus moisture vertically and calorific value horizontally, the writer constructed the diagram shown in Fig. 1, no corrections being made for variations in the amounts of sulfur and nitrogen present.

In the higher rank coals, which contain little moisture, the groupings produced by the graphic method employed in Fig. 1 were essentially identical to those obtained by classifying the same coals by either the Seyler or the Parr system. In the lower rank coals, the increasing amounts of moisture retained in the air-dried sample progressively increased the volatile matter plus moisture coördinate and decreased the calorific value coördinate, as compared to groupings made on the dry coal basis. As a result the curve was so extended as to make possible an almost wholly satisfactory chemical definition and distinction of the low-rank coal types proposed by Ashley. It is moreover true, as would be expected, that, in Fig. 1, in the lignite, subbituminous, and bituminous ranks, the canneloid coals fall above and to the right of the normal coals, whereas very woody coals, such as that from Williston, N. Dak., fall below the normal coals. With increasing metamorphism and an approach toward the semibituminous rank, the cannel-coal curve approaches that of the normal coals; and in the semibituminous field apparently crosses the curve of the normal coals, presumably due to the distillation and

[4] S. W. Parr: The Classification of Coal. *Indus. & Eng. Chem.*, **14**, 919.

[5] M. R. Campbell: The Coal Fields of the United States: General Introduction. U. S. Geol. Surv. *Prof. Paper* 100-A (1922) 33.

elimination of some of the highly hydrogenous constituents present in lower rank cannel coals.

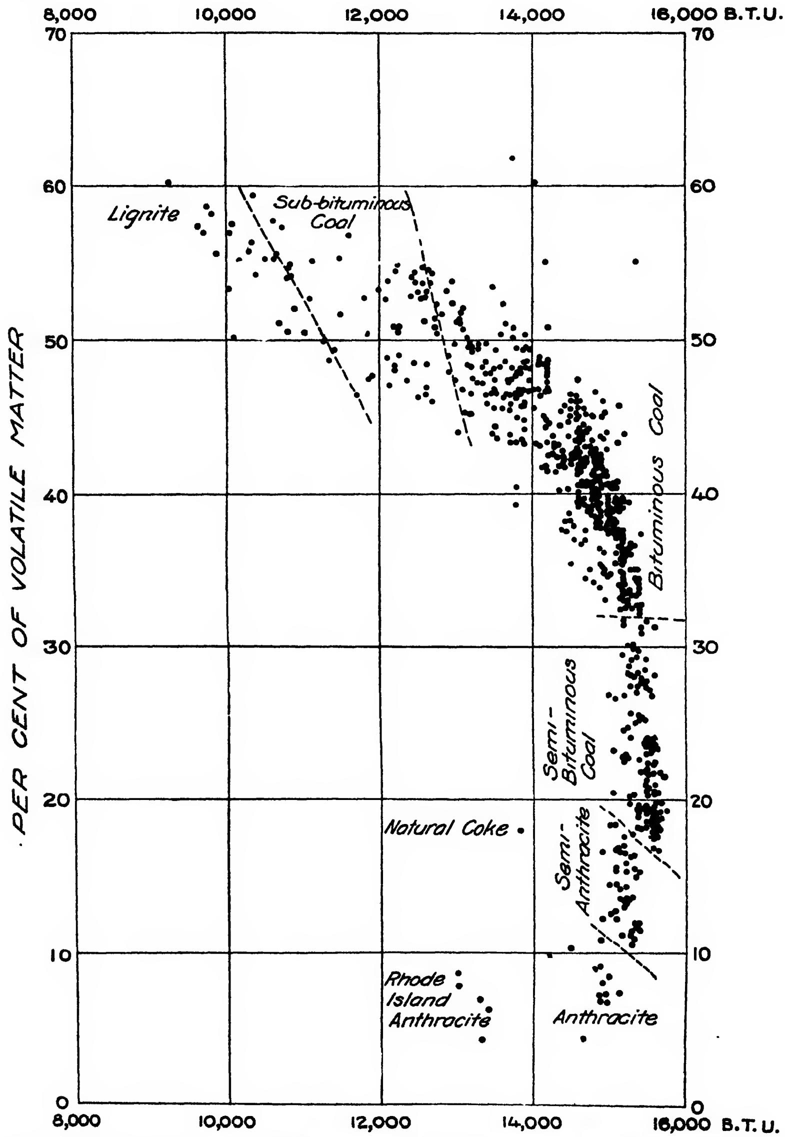

FIG. 1.—VOLATILE MATTER (MOISTURE PLUS VOLATILE MATTER) AND CALORIFIC VALUE OF COALS REPRESENTATIVE OF COAL RANKS AS NOW RECOGNIZED BY THE U. S. GEOLOGICAL SURVEY. ANALYSES PLOTTED ARE ON AIR-DRIED, ASH-FREE BASIS.

The principal anomalies that remained in the groupings shown by Fig. 1 exist in the high-sulfur, high-moisture coals of the interior fields. These anomalies may be due to anomalous properties of the coals themselves,

but certain other considerations strongly suggest that they are due to the presence of disseminated gypsum in the coal, which was not recognized by the analyst, and was not allowed for in the calculation of the ash content of the coals as reported in the analyses.

For the successful application of a scheme of classification, such as that used in constructing Fig. 1, it is essential that a standard analytical procedure be followed, in order that results may be comparable. It is even more important, especially for the lower rank coals, that the utmost care be taken in the collection and shipment of samples for analysis. Lignites and subbituminous coals are so unstable that marked alterations in their chemical composition take place during an exceedingly brief exposure to the air, so it is most important that samples of lignite or of subbituminous coal taken for analysis be cut at strictly fresh working faces. Coal taken from a fresh face may show several per cent. more volatile matter and several hundred more British thermal units calorific power than rib coal from the same mine collected after being exposed to the air for a few days.

It also must not be forgotten that the degradation of low-rank coals, which speedily ensues on their direct exposure to the air, may to a degree be paralleled by geological processes operating through long periods of time. For example, it seems probable that oxygenated artesian waters cause chemical changes in coal beds along which they percolate, and that a more rapid oxidation of coal beds occurring above ground-water level in arid regions may be caused by the air dissolved in descending meteoric waters.

Summary

The development of a satisfactory classification of coal on chemical criteria necessitates an agreement on:

1. A geological and chemical definition of unweathered coal.
2. Adoption of a more reliable method for the collection and shipment of coal samples.
3. The adoption of rigorously uniform methods of coal analysis.
4. The testing of coal samples for carbonate and sulfate impurities, present as unstable components of the ash.

Also, it is, in the writer's opinion, essential to the formulation of a scientific and systematic classification of coal on a chemical basis that all moisture forming a normal and essential part of coal, as it is found in nature, be recognized and reported in analyses as a component of the coal and not as an extraneous impurity to be excluded from consideration. The utilization of the air-dried form of proximate analysis appeals to the writer as the best method of discriminating between water accidently present in the coal sample and moisture to be regarded as a natural constituent of the coal.

DISCUSSION

A. C. Fieldner, Pittsburgh, Pa.—This is a very practical system for classifying coal. The use of percentage of moisture plus volatile matter and moisture-and-ash-free heating value as criteria for classification afford practical measuring sticks that are at hand in any commercial coal laboratory. The only drawback is in using moisture in air-dried coal as a physical constant of the coal. Coal laboratories do not maintain any special apparatus in which to make air-dry determinations. These determinations are made either by exposing thin layers of the coal to the action of the atmosphere, or by placing the coal, in a thin layer, in an air-drying oven in which air is circulated over the coal at 5° to 10° above room temperature for approximately 24 or 48 hr. The humidity is not controlled; it may vary considerably. These differences in humidity cause rather large variations in subbituminous coal and lignites. Humidity conditions at one period may give 20 per cent. moisture in the air-dried coal; at another time, with higher humidity, it may be 25 per cent. or even more. Therefore for strictly comparable work laboratories should determine moisture in the air-dried coal at a definite temperature and humidity. These variations are most noticeable in subbituminous coals and lignites; they do not seriously affect low-moisture bituminous coals.

S. W. Parr, Urbana, Ill.—We are all impressed with the close relationship between the moisture content of any type of coal and the rank. The Illinois field extends from southeast to northwest, perhaps a distance of 300 miles. The southern Illinois coals, as we speak of them, have a moisture content of 8, 9, or 10 per cent., and the Indiana as low as 4 or 5 per cent.; in Montgomery County, they contain even 17 per cent. moisture, which parallels the type. That is not the right word, because there is so little variation in the real coal; but it characterizes what we know to be the value of those coals for general use. Saying nothing about having to pay for more water in one case than the other, the low-moisture coals are high-carbon coals and behave much better in domestic appliances.

This matter of moisture content is misleading if we take the whole field. One of the students in the Engineering Department of the University of Illinois carried on a little research along this line. He determined very carefully the specific gravity of a block of coal and then allowed the block to air dry and took the specific gravity as the moisture content went down; its specific gravity became less and less. Then he put that same coal in water and let it stand a given length of time when he determined the specific gravity and found it was the same as when the

coal came from the mine. I am more and more inclined to look upon moisture as moisture, which varies with circumstances.

In December, a couple of pounds of coal was sent to us from New Mexico, it was anthracilitic, or whatever you wish to call it. It was beautiful clear coal, conchoidal fracture, and I think was sent from the belief that it was anthracite, especially because, among other peculiarities, it had only 2 per cent. moisture. A coal of that kind, hard, with that appearance and fracture, and 2 per cent. moisture, you will be justified, in saying, is pretty apt to be anthracite. But referring to its calorific value on the unit coal basis, that coal is clearly a subbituminous, and would come in the second division, below 14,000 B.t.u. per lb., and clear down at the bottom of the chart with 2 per cent. moisture instead of up among the lignites or subbituminous coals. It had the oxygen content of 18 or 19 per cent., and absolutely no coking property.

The Southern Utah coals, of which we have quite a good many, run to 4 per cent. moisture and are of exactly the same type. Not long ago we received coal from Northern Siberia, which was beautiful material, less than 4 per cent. moisture, but a lignite. That is subbituminous in a way. So these may be low-moisture characteristics with very high oxygen and very clearly given their rank by the colorific value.

Clarence A. Seyler, Swansea, Wales.—It is well known that lignitic coals have the power of holding a considerable amount of moisture. In fact, it is quite possible to make use of this properly in the classification of coals, as has been done by Doctor Ashley, who uses the fixed carbon (100—volatile matter plus moisture) in the moist sample to arrange coals in a continuous series according to rank. I do not think, however, that this is the best way of classifying coal, for many reasons. First, the moisture of "air-dried coal" is not a definite thing unless the temperature and humidity of the air are specified, and I do not think that data on this basis exist. Until they are available, it is not possible to make any accurate classification in this way. The moisture being so variable, one is inclined to regard it as accidental and not essential to the coal substance, and I much prefer Doctor Parr's basis of "unit coal," which is now generally accepted. By using it in conjunction with the ultimate analysis, one can get a very satisfactory classification for scientific purposes, and it may be possible to bring it into relation with a use classification based on volatile matter and moisture.

Note.—At a meeting of the American Section of the Coal Research Club on the evening of this meeting I discussed the whole subject of classification and suggested a joint pronouncement on this subject from the American and British chemists, which I hope will mature shortly.

W. T. Thom, Jr.—It is very desirable that a technique be perfected which will permit of a division of moisture reported in coal analyses

between that which is definitely related to the composition of the coal and that which is present as purely accidental moisture. It appears that the low-rank coals contain moisture which is related to, or a reflection of their chemical or physical constitution, just as the calorific value of the coal is a weighted reflection of the several factors entering into the aggregate composition of the coal.

A. C. Fieldner.—Has the author made any tentative plots in which total as-received moisture was used instead of air-dried moisture?

W. T. Thom, Jr.—No, though I can readily do so with the material in hand. It is my thought, however, that variations in mine conditions would cause notable variations in moisture in the sample as received, the result simply of variations in the amount of water accidentally included in the sample as cut in the mine.

In adding together moisture and volatile matter, as given by the "air-dried" analysis, I felt that in a way I was canceling variations that result from slight differences in analytical practice. That is, under some conditions the moisture reported will be unduly high and volatile matter correspondingly low, and vice versa, the two variations being roughly compensating.

A. C. Fieldner.—I question whether it would not be better to use the total as-received moisture of the coal as it occurs in the seam excluding incidental surface moisture. The objection to this method would be that in some cases the surface moisture of the coal could not be kept out of the sample. Likewise, coal that has been mined and exposed to the weather for a short time would have lost a material portion of the seam moisture. Such coal could not be brought back to the true total moisture content. It would be easier to bring it into a standard air-dried condition.

R. D. Hall, New York City.—Is it not the correct way of ascertaining the true character of the coal to add moisture to it and then dry it by a standard method so that if it has in transference or in the bed been subjected to conditions of drying that are not standard this will be corrected in the laboratory. All the accidental moisture will be out and all the moisture natural under the conditions will be in the coal. The air drying should be at a given temperature and the drying air should have a given moisture content.

Mascot, Tennessee, Zinc Area

By Wilbur A. Nelson,* Nashville, Tenn.

(Birmingham Meeting, October, 1924)

In 1839, Gerard Troost,[1] the first State Geologist of Tennessee, reported the occurrence of zinc ores in east Tennessee, in connection with the iron ores at Embreeville; in 1844,[2] he refers to the zinc deposits of east Tennessee, especially the apparently rich deposits occurring in Jefferson and Claiborne Counties, while his ninth annual report[3] is a description of the zinc deposits of Jefferson County and a description of the most improved processes by which zinc is extracted from its ores. Yet, only during the last few years have these ores been successfully worked.

As far as can be learned, prior to the systematic development of the Mascot district in 1911, no large-scale or successful operation of any of the zinc deposits was carried on. But in that year, after several companies had made considerable progress in developing the Mascot area and had proved a relatively extensive body of low-grade sulfide ore, the American Zinc Co. entered the field. It introduced modern methods of prospecting and mining and from the first was successful. Too great credit cannot be given this company for its pioneer work in a previously unimportant field. Throughout the history of its operations, the American Zinc Co. has confined its efforts to underground mining of the sulfide ore, sphalerite. This company has found that successful results in zinc mining in east Tennessee can be achieved only by expending large sums in prospecting and blocking out bodies of pay ore in sufficient magnitude for large-scale operations.

At Mascot are located the mines of the American Zinc Co. of Tennessee, the mines being situated along the Southern Railway in the Holston River Valley, Knox County, about 13 miles northeast of Knoxville. At first only open pits, which were worked for oxidized ores, were operated and the production was small. In 1900, the Roseberry Zinc Co. was organized and sank to a depth of 187 ft. what is now known as No. 3 shaft of the American Zinc Co. The upper 30 ft. was in residual clay,

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* State Geologist.

[1] Fifth Annual Report, Tenn. Geol. Surv., 41.

[2] Seventh Annual Report, Tenn. Geol. Surv., 43.

[3] Ninth Annual Report, Tenn. Geol. Surv. (1848).

the remainder in brecciated and massive dolomite. Ore was encountered at a depth of 104 ft. Short tunnels were driven from the base of the shaft to tap the orebody but most of the production of the Roseberry company was derived from the large open cut (No. 3), located on the west bank of Roseberry Creek. Both carbonate and sulfide ores were mined. A few years later, the property was purchased by the Grasselli Chemical Co. and, in 1915, by the American Zinc Co.

In 1903, the Holston Zinc Co. began operations in both carbonate and sulfide ores just west of the Big Flat Creek; its workings are now known as No. 1 open cut of the American Zinc Co. A shaft was sunk to a depth of 170 ft., 670 ft. north of the present No. 1 shaft of the American Zinc Co. This shaft was later abandoned. It is said that ore was found from the 120-ft. to the 160-ft. level. Both the Roseberry and Holston companies carried on extensive prospecting by drilling. Mills for crushing and concentrating the ore were erected by each company and operated for a short time.

In 1911, the American Zinc, Lead, & Smelting Co. entered Tennessee, and, under the name of the American Zinc Co. of Tennessee, acquired the property formerly owned by the Holston Zinc Co. Its output consists of sulfide ore only and it is the only company in Tennessee continuously engaged in mining the sulfide ore of zinc. The present holdings of the American Zinc Co. consist of 3200 acres of land in Knox County and 400 acres in Jefferson County. The orebody has been developed for 7900 ft. along the strike and for 1200 ft. down the dip.

Production

No accurate figures of the zinc production of east Tennessee prior to 1912 are obtainable, but the output in those years was small. Since 1912, the production as reported by the United States Geological Survey is as follows:

East Tennessee Zinc Production since 1912

Years	Mine Production (Crude Ore), Short Tons
1912	32,347
1913	171,392
1914	357,437
1915	525,829
1916	702,326
1917	883,341
1918	598,742
1919	649,844
1920	598,742
1921	319,764
1922	411,484
1923	579,022

The rapidly increasing output after 1912 was due to the operations in the Mascot district, which furnished almost the entire production until the Embree Iron Co. started producing ores, in 1919. The peak of production was realized in 1917, when 883,341 tons of crude ore were mined, and east Tennessee ranked seventh among the producing districts of the United States. Since then, lower prices and a decreased demand have caused a falling off in production.

General Geology and Structure

A study of the general geologic condition of the 50-mile area around the Mascot zinc district shows many interesting facts, which may have a general bearing from a geologic standpoint on the occurrence in commercial quantities of zinc in this area.

This is the home region of Appalachian structure, with closely folded rocks, practically all of which dip to the southeast with varying degrees of steepness, 20° to 30° being the average dip, except in close proximity to the numerous roughly parallel faults, where the beds are generally nearly vertical or overturned.

The formations, mostly of Cambrian, Ozarkian, Canadian or Ordovician age, were laid down in long, narrow, trough-like seas, and as one of these seas was gradually filled with sediment, during geologic time, the old shore line advanced westward and the ancient streams dumped sediment into a similar trough-like sea lying just to the west of the one just completely filled by sedimentation. At certain periods these narrow parallel seas were connected by passages, with the result that certain formations were deposited in all of them; but at other periods the oscillatory nature of the earth's crust cut off these passages and a particular type of filling by sedimentation would only start in the most eastward sea then existing.

It would appear that Copper Ridge, situated 9 miles northwest of Mascot, was one of these old land barriers, for on this ridge only the earliest formations of the Blount group of the Ordovician age were laid down, while in the troughs, or seas, to the east several hundred feet of older Ordovician rocks were formed. Just to the east of Copper Ridge came in the great Clinch Mountain trough or sea, which was one of the most persistent seas of ancient east Tennessee, having, during the periods following the Ordovician, that is, during Silurian and the following ages, an outlet to the north, with a probable head of this narrow gulf in the region of Corryton, about 6 miles northwest of Mascot. To the east of the Clinch Mountain trough, is the Holston River high or barrier, so named because along and on top of this old buried ridge the Holston River now meanders. Mascot and the zinc deposits of this area are located on this ridge.

Indications point to the fact that this ridge culminated in the area about 6 miles north of New Market and was less marked to the southwest in the vicinity of Knoxville. All of this ridge was an old high area, but probably not as marked a high as Copper Ridge. The area occupied by this old ridge is one of the largest areas in east Tennessee covered by unfaulted dolomites. One way to account for this fact would be to consider that this old ridge is probably covered by an abnormal thickness of massive beds, such as the dolomites of Canadian and Ozarkian ages, and that this old high existing at this point in Cambrian times probably did not permit of a good development of the underlying massive sandstones of the Rome formation, which sandstones are the thrust-carrying strata of the east Tennessee valley region.

The highest ancient ridge of the Holston River high must have been along its western edge and close to the eastern edge of Clinch Mountains, for the sequence of formations in those troughs or ancient seas to the east of this old ridge is greatly different from the sequence in the troughs to the west. Although this ridge may not have been as high as the Copper Ridge high, it was a much more effective barrier and one through which it would appear that there were no channels leading to the west, as the Athens shale occurs in all those troughs to the east of the Holston River high and in none of the troughs to the west.

After the filling in of the Athens trough, which is the first trough east of Mascot, there must have come a period of cross-folding or a period in which a new system of erosion was developed which so modified the configuration of the earth's surface as to permit the development of channels through the succeeding western ridges of the east Tennessee valley region.

The beginning of cross-folding, which culminated in the cross-faulting now seen extending through Coal Creek, Anderson County, 28 miles northwest of Mascot, may have had its inception at the time of the laying down of the Blount group of the Ordovician. The location of this cross-folding and faulting may have been caused by a thinness of the Ordovician, Canadian, Ozarkian, and Cambrian sediments deposited in the heads of several of the trough-like seas, which are on a line between Coal Creek and Knoxville, as the excessive thinness of these formations might produce a line of weakness along which folding and shearing might be expected to take place first, as the forces that produced the thrust faulting, which forces came from the ocean, increased in magnitude and intensity.

The foregoing deductions on the manner in which these Paleozoic formations that now cover the surface of this section were deposited, consolidated, and folded, contain many factors that should be considered in studying the causes and reasons for the present occurrence of zinc ores in the rocks of this region.

The old idea of the indivisibility of the Knox dolomite must be forgotten, for this formation can readily be subdivided. It is made up of varying formations, described by Ulrich.[4] This dolomite series, which includes in places beds of limestone, and which varies from place to place due to thickening, thinning, or even complete absence of one or more of the formations of which it is composed, is our representative of two complete geologic ages, the Canadian and the Ozarkian.

Detailed study of this series in east Tennessee shows that at several horizons there are well-formed sedimentary breccia layers, several feet in thickness, made of fragments of chert, quartz, limestones, and dolomite, as well as brecciated horizons formed by earth movements. The sedimentary breccia horizons occur at contacts between some of the different formations making up this dolomite series, which has a thickness of 2400 to 3600 ft., while the other brecciated horizons occur along lines of weakness in this rock series.

The mining developments at Mascot are on the western limb of one of the largest synclines in east Tennessee, which is 5 miles wide and faulted on both sides. The horizon at which the Mascot ore occurs is downfaulted on the eastern limb of the syncline and does not come to the surface. The average dip of the strata of the mines is 20° to the southeast. Minor flexures and warpings cause local flattening, steepening, or even reversal of the prevailing dip. The orebody appears to parallel the bedding plane of the dolomite and, therefore, its dip conforms to the regional dip, which varies from about 10° to the southeast to vertical. No faults of great displacements have been discovered in the mining operations, but minor breaks, which may be measured in inches or fractions of an inch are numerous; some of these have occurred since the mineralization of the region.

In the Mascot region, study of the old Knox series shows that this group can easily be divided into two distinct formations; a further detailed study may show that even further definite division lines can be found and mapped. Just a short distance below the outcrop of the brecciated zinc-ore horizon in the old Roseberry open cut, there occur a few feet of very irregular wavy bedded dolomites, which show that they were deposited on an old irregular land surface, filling up the irregularities of the old surface, which is the contact between the Ozarkian and Canadian rocks. The exact contact occurs 10 to 20 ft. below these wavy beds, but is not exposed at this place. The top of these wavy beds is 20 ft. below the base of the brecciated zinc horizon in the Roseberry mine, and as these wavy beds probably have a thickness of 10 to 20 ft., the zinc horizon can be considered to occur at practically the base of the rocks of Canadian age, near one of the great unconformities of east Tennessee.

[4] E. O. Ulrich: Revision of the Paleozoic. *Bull.* Geol. Soc. of Amer. (1911) **22**, 281-680.

The Canadian age is represented in Tennessee by the Powell, Cotter and Rubideaux formations.[5] A study of the Mascot area indicates that only one of these formations is present, the Cotter, which has a thickness of 1100 ft. But sufficient detailed work has not been done in the Mascot area to show positively if any other of the Canadian formations are present. The zinc ores occur in a brecciated zone near the base of this formation. The Canadian is here composed of a series of interbedded dolomites and limestones, containing chert that on weathering becomes finely divided and breaks into sharp angular pieces that tend to be flinty and generally red-stained.

The topmost beds are composed of layers of magnesium limestone, dolomite, and pure limestone, lying unconformably below a very pure limestone known as the Mosheim formation. In the Canadian at Mascot, there occurs, as usual at irregular intervals in the formation, layers and nodules of partly flinty chert and occasionally a layer ¼ to perhaps 1 or 2 in. thick of rounded glassy sand grains. Drill records show that such thin sand stringers occur at 75, 235, 265, and 320 ft. above the top of the ore horizon, while a very marked, 1-in. sand-grain horizon scattered in the dolomite occurs 33 ft. below the orebody. If rounded sand grains occur in the upper part of the Canadian at this point, they have not been seen. Very detailed examination of the entire 1100 ft. of the Canadian has not been made, yet from the examination made, rounded sand grains occurring in stringers in the dolomite have been found only in the lower 500 ft. of this series. Likewise, in the lower part of the series, particularly below the ore bed, there occurs considerable white, translucent primary chert, occurring in long, thin, banded stringers parallel to the bedding, but no great thick masses of chert were seen in the Canadian. At 70 ft. below the orebody, there was seen in the I-H crosscut of Mine No. 2, massive white chert, which is probably Ozarkian chert, occurring at the top of this series of rocks.

The Ozarkian rocks are quite distinctive and produce a chert that is quite a different type than that of the Canadian. The chert in the upper part of the Ozarkian occurs in great irregular ledges and masses several feet thick and undoubtedly represent primary chert augmented greatly by secondary chert, which started forming during the land period interval that existed in this area in early Canadian time. These great masses of chert are distinctive in appearance, being white in color, very hard and tough and irregularly cracked and checkered, but only to a slight degree where exposed to weathering.

The Ozarkian has a thickness of approximately 1660 ft. at Mascot. This massive white contact chert extends down into the formation for 50 ft., more or less, then there occurs, in large masses, throughout the next

[5] E. O. Ulrich: Personal communication, June, 1924.

550 ft. a very characteristic white sugary chert; below this point, particularly throughout a 225-ft. thickness of beds starting 350 ft. above the base of the Ozarkian, the chert is of a most perfect oolitic variety, which occurs in stringers several inches thick and is of an opaque whiteness. This oolitic chert registers a condition of original deposition and may not, in other areas in east Tennessee, be characteristic of this part of this formation. The lower 350 ft. of this series contain a few 1- and 2-in. layers of sandstone, composed of coarse white grains, closely cemented and also occasional layers, several inches thick, of massive white chert.

As the Ozarkian and Canadian series weather readily, it is seldom that the rock layers are seen except along stream banks; on this account particular attention must be given to the type of chert these formations produce on weathering, as it is only by a study of these cherts and the fossils they contain, that the different formations can be recognized, under the general conditions existing in east Tennessee.

Ores and Associated Minerals

Minerals

The chief ore mineral of the mine is sphalerite. Near the surface and in solution channels where oxidation has taken place, the sulfide has been altered to smithsonite and calamine. Most of the sphalerite of the Mascot mine is extremely light yellow in color. It occurs in the brecciated horizon as veinlets, irregular masses of variable size, fracture fillings, and breccia cement. Gangue minerals occurring with the sphalerite are dolomite and calcite. The quantity of sphalerite is variable, generally being greater in the more intensely brecciated rock. A complete report on the zinc deposits of east Tennessee, by Mark H. Secrist, has just been published by the Tennessee Geological Survey as Bulletin No. 31. The following facts in regard to the minerals occurring at Mascot are quoted from this bulletin:

> A carbonaceous compound sometimes occurs along fracture planes: also occasional pockets of masses of barite are found. The gangue consists almost entirely of dolomite, calcite, and the country rock. Microscopic examination of thin sections of the ore show that the country rock consists of fine-grained, anhedral crystals of dolomite, which are mutually interlocking and possess, in general, well-developed rhombic cleavage. The average diameter of the grains is about 0.10 mm.
>
> Minute isolated grains of pyrite, frequently altered to limonite, are disseminated through the country rock and tend to occur in the interstices between individual crystals.
>
> The vein, or replacement, minerals have been deposited in the following order: Dolomite, sphalerite, pyrite, dolomite, when present. The vein dolomite is coarsely crystalline and shows good rhombic cleavage. Generally the contact of country rock and dolomite is well defined and clearly shows replacement of the former by the latter, but a narrow seam of limonite frequently obscures the actual contact and has partly corroded the edges of the crystals adjacent to it.

That the contact zone of the country rock and dolomite was readily susceptible to replacement by later minerals is evidenced by the presence of variable amounts of sphalerite and pyrite. The pyrite occurs in small grains, many of which show distinct crystal outline and, locally, complete replacement of the earlier minerals has resulted in the formation of short, discontinuous veins of pyrite.

The mode of occurrence of sphalerite is similar to that of pyrite, in that it tends to be more abundant in the contact zone of country rock and dolomite. Small, disconnected masses of sphalerite, with veinlets protruding along interstitial openings between crystals, or along their cleavage cracks, occur promiscuously throughout country rock and dolomite and locally attain a considerable size.

Where pyrite and sphalerite are in contact, the order of deposition is frequently not clear although some unmistakable evidence of pyrite invading along cleavage cracks of sphalerite and replacing that mineral are apparent.

PARAGENESIS

Country Rock
Dolomite
Sphalerite
Pyrite
Dolomite, when present

The Mascot Ore Horizon

As already stated, it is considered that the zinc-ore horizon at Mascot occurs about 40 to 60 ft. above the top of the Ozarkian series and in the base of the rocks of Canadian age, in strata that can be considered as belonging to the latter formation. The ore does not occur continuously along the strike of the rocks in the zone just above the contact between the Canadian and Ozarkian, but occurs in shoots irregularly spaced. These oreshoots vary from 100 to 200 ft. in width and are an intensely brecciated zone varying from 25 to 120 ft. in thickness. The ore in these brecciated shoots varies in richness, containing from 1 to 5 per cent. metallic zinc. These shoots are irregular, tortuous, and more or less connected. Their distribution is irregular. In practically every case, the bottom of the oreshoot extends farther up or down than the top of the shoot. The thinning down of the ore takes place from the hanging-wall side of the orebody. However, there is no definite hanging and foot wall to this orebody, as such terms are used in other mining districts.

In general, the following sequence is found in Mine No. 2 of the American Zinc Co., in the rocks above and below the orebody. Starting on the upper side of the orebody, the hanging wall is a fine-grained gray dolomite that, in a few places, contains a mass of 1- to 4-in. chert nodules occurring as a layer in the dolomite and forming the boundary of the ore. Then occurs the irregular orebody, having for its foot wall a series of bedded brown dolomites or their replaced or altered equivalent, the replaced equivalent being crystallized gray limestone.

Below this foot wall, which is often about 10 ft. thick, occurs another brecciated horizon that is, as a rule, barren, or carries only small amounts

of zinc. This lower brecciated horizon varies in thickness as much as the ore-bearing brecciated zone. Below the lower brecciated zone there also occurs at many places in the No. 2 mine of the American Zinc Co., a bedded series of brown dolomites, which contain a fairly persistent 1-in. layer of rounded, glassy, sand grains, about 10 ft. below its top. Chert nodules and 1- to 2-in. chert bands occur in the bedded dolomite, starting a few feet below the horizons of the glassy sand grains, and occur throughout the rest of the dolomite series down to the top of the Ozarkian.

The extent of the main orebody is not definitely known, as prospecting is still being carried on. An orebody of commercial grade has been proved to extend from Roseberry Creek, on the west, to a point ½ mile east of Mascot Station, a distance of ¾ mile. Intensive drilling has been carried on over this area, both along the strike and down the dip. It is reported that this drilling indicates the orebody to be roughly lenticular in shape, although its limits down the dip have not been reached. Within the mineralized zone there is considerable variation in the zinc content, as can be observed from the manner in which the ore occurs in pockets that follow no definite direction. The American Zinc Co. has mined only those areas or pockets that contain the highest grade of ore. The intervening ground has been avoided, although it is not absolutely barren and may even contain small but high-grade masses of ore.

Origin of the Ore

The time available for the writing of this paper has not permitted the reaching of any definite conclusions as to the origin of the Mascot zinc ores, and although the conclusions reached by Secrist[6] do not appear to account fully for all phases of this interesting ore deposit, these conclusions will have to be accepted until further work on this problem proves, modifies, or disproves them. Mr. Secrist's conclusions are as follows:

> The zinc ores of east Tennessee were not originally deposited in the manner in which they now occur but represent a concentration in local areas resulting, in general, from solution, transportation, and redeposition by circulating ground waters.
>
> Except where ore has undergone superficial alteration and oxidation, the zinc ores consist of the zinc sulfide—sphalerite. This occurs disseminated in the limestone or dolomite both as a replacement of the rock and as the cement in brecciated beds. As a rule, the process of replacement has played an important role in the ore formation. Breccia fragments sometimes show solution and replacement by both ore and gangue minerals. But again, the breccia fragments are extremely sharp-angled and show no replacement. In such cases, the minerals are confined entirely to the matrix or breccia cement. Both types of ore are widespread and grade into each other. No instances were observed in the field where only one type of ore occurred.

[6] Mark H. Secrist: Zinc Deposits of East Tennessee, Tenn. Geol. Surv. *Bull.* 31 (1924) 31.

As has been repeatedly stated, the ore is associated with brecciated horizons in the country rock. The origin of the brecciation is not at all times clear, particularly when no visible planes or movement can be seen. On the other hand, at the Felknor mine, the Fall Branch mine, New Prospect, etc. direct evidence of brecciation associated with faulting is at hand.

The breccia is usually made up of sharp-angled fragments of the country rock cemented by a matrix, which consists of variable amounts of white or gray dolomite, some calcite, chert, sphalerite, galena, and pyrite. It should be mentioned that galena is found only in a few districts and is not a widespread constituent of the breccia filling. In some localities, notably at Friendsville, Eye Mills and Fall Branch, considerable quantities of barite are associated with other minerals in the breccia; thus the complexity of the ore varies at different localities. At Mascot, practically no minerals other than sphalerite, dolomite, small amounts of calcite, chert and pyrite are found.

As is typical of breccia or broken-ground deposits, not all parts of the brecciated horizons are mineralized but the ore is distributed in bodies or pockets, in random fashion in the horizons. Such localization entails great uncertainty in mining operations where advance prospecting to determine the extent of the richer bodies has not been employed.

Ducktown, Tennessee, Copper District

By Wilbur A. Nelson,* Nashville, Tenn.

(Birmingham Meeting, October, 1924)

All of our accounts say that the discovery of copper ore at Ducktown, Tenn., was made in August, 1843, yet it would appear that samples of copper from this district were found by DeSoto, when he wandered into southern Tennessee, in 1539, in his four years of exploration through the Southern States. The following quotation is taken from his diary:

"Towards the north there was a province named Chisca; and that there was a melting of copper, and of another metall of the same colour, save that it was finer, and of a farre more perfect colour, and farre better to the sight, and that they used it not so much, because it was softer. And the selfe same thing was told the governor in Cutifa-Chiqui, where we saw some little hatchets of copper, which were said to have a mixture of gold. But in that part of the country it was not well peopled; and they said there were mountains, which the horses could not passe; and for that cause, the governor would not goe from Cutifa-Chiqui directly quicker."

DeSoto sent two of his company to try to find these mines, but after five days' wandering through the mountains they returned, stating that their guides had become lost. Although the Ducktown area may have been known to the ancient Indians, the copper deposits were actually discovered in August, 1843, when a Mr. Lemmons, while panning for gold on Potato Creek, in the Ducktown basin, found some reddish-brown decomposed rock. His disgust on finding that this yellow metal was not gold was so great that he did not try to develop his find. In March, 1847, B. C. Dugger erected an iron forge at this same place, but was unable to work the iron as it contained so much copper that on cooling it would break to pieces. The finding of copper in the iron ore by Mr. Dugger led to further explorations; and in April, of the same year, A. J. Weaver, who was passing through that country, told the people that the black rocks they had dug out were rich copper ore. Mr. Weaver began the

* State Geologist.

first mining in this district. This account of the actual finding of copper in Tennessee is described by both Currey[1] and Safford.[2]

It was not until 1850 that general attention was attracted to this region and mining operations were started. Five years later, in 1855, 14 mines were in operation and, by September of that year, these mines had produced and shipped 14,291 tons of ore, worth more than $1,000,000. Only the "black copper" ores, products of secondary enrichment from beneath the gossan outcrops and overlying the massive sulfide deposits, were then mined and smelted for their copper content. After the exhaustion of this ore, which was about 1889, the operators developed a process of treating the unaltered pyritic ores. This process consisted of open-heap roasting, followed by blast-furnace smelting; which method was used until 1903.

Shortly after 1900, the companies operating in this district were compelled to erect acid plants to prevent the escape of the sulfur dioxide produced in the smelting operations. The Tennessee Copper Co., of Copperhill, started its plant in 1906; the Ducktown Copper & Iron Co., of Isabella, started to build its plant in 1908. Both plants were started for the purpose of relief from the damage done to vegetation in the surrounding country by the sulfur fumes and to utilize the valuable constituent of the ores that had previously gone to waste. Acid making was started by the Tennessee Copper Co. about Dec. 1, 1907; and from that date the Ducktown basin has been a continuous producer of sulfuric acid. The plant of the Ducktown Sulphur & Iron Co. was put in operation on June 11, 1909.

At present, three mining companies are operating in the Ducktown basin; these are the Tennessee Copper Corpn., operating the Burra Burra and London mines; the Ducktown Sulphur & Iron Co., the chief operation of which is the Mary mine; and a new company, the Ocoee Copper Co., which has developed a mine joining the old East Tennessee mine, and which has in addition leased, for 10 years, the old East Tennessee mine from the Ducktown, Sulphur Copper & Iron Co.

Location

The Ducktown district is in the extreme southeastern corner of Tennessee; the principal mines are within a few miles of both the Georgia and the North Carolina state lines. The district is served by the Blue Ridge division of the Louisville & Nashville Railroad, and is half way between Knoxville, Tenn., and Atlanta, Ga. The principal railroad points in the Ducktown basin are Copperhill and Ducktown. The area is included in the Ducktown special map of the U. S. Geological Survey.

[1] Richard O. Currey: "Geology of Tennessee," 70–82. (1857.)

[2] James M. Safford: "A General Reconnaissance of the State of Tennessee," 59–68. (1856.)

Production

This district, in late years, has had a more or less steady production. During the dull period of 1921, when most of the large western mines were closed, the demand for sulfuric acid was sufficient to keep the Ducktown smelters operating at nearly full capacity. The production of copper from this district since 1920 has been:

	Pounds		Pounds
1920	16,727,803	1922	13,979,031
1921	15,084,294	1923	18,948,969

The total production, to the end of 1923, is said to be 431,481,000 lb. The figures on production of sulfuric acid for this district are not available, although the production and selling of this byproduct of the copper mining is one of the most important activities of this district.

General Geology and Structure

The Ducktown copper deposits were first described by Safford,[3] in 1856. In recent years, they have been described by Henrich,[4] Kemp,[5] Weed,[6] Emmons and Laney,[7] Taylor,[8] and Gilbert.[9] The following general résumé of the geology and structure of this region is taken from these different articles; from the work of the U. S. Geological Survey in adjoining areas; and from information obtained by the author on several visits to this region. The best description of the formations and important features of the geologic history of this region as a whole is given in the Nantahala Folio.[10]

Ducktown lies in the Unaka Mountain province of Tennessee and just east of the great valley of east Tennessee, which is part of the geological province known as the Appalachian Valley. The Ducktown basin is composed of a series of metamorphosed sedimentary schists. These rocks are known as the Ocoee series, but their age is not definitely known; some of them may prove to be of late Paleozoic age. The prevailing rocks are sandy schists and graywackes with interbedded mica schists. The most prominent beds are the metamorphosed phase of a series of

[3] *Op. cit.*, 63–66.

[4] C. Henrich: Ducktown Deposits and Treatment of Ducktown Copper Ores. *Trans.* (1895) **25**, 173.

[5] J. F. Kemp: Deposits of Copper Ores at Ducktown. *Trans.* (1902) **31**, 244.

[6] W. H. Weed: Copper Deposits of the Appalachian States. U. S. Geol. Surv. *Bull.* 455 (1911).

[7] W. H. Emmons and F. B. Laney: Mineral Deposits of Ducktown, Tenn. U. S. Geol. Surv. *Bull.* 470 (1911).

[8] J. H. Taylor: Pyrite and Pyrrhotite Resources of Ducktown, Tenn. *Trans.* (1918) **59**, 88.

[9] G. Gilbert: Oxidation and Enrichment at Ducktown, Tenn. *Trans.* (1924) **70**, 998.

[10] Arthur Keith: U. S. Geol. Surv. *Geol. Atlas*, Nantahala Folio (1907).

sedimentary beds of sandstones, conglomerates, grits, and shales. Most of these beds are highly siliceous. However, the most characteristic feature of the whole series is the lack of effective sorting of the material making up these beds, both as to size and composition. The rocks have undergone close folding, some thrust faulting and severe metamorphism, and both bedding and schistocity approach the vertical. The structure of this region has been worked out by the different mining companies and various folds and faults have been mapped.

According to Emmons, thin lenses of limestone were deposited in the great series of sedimentary rocks whose metamorphosed equivalents occupy the Ducktown area. At no place on the surface in this district are such limestone beds exposed. In the lower levels of the old East Tennessee mine, limestone is said, by Emmons, to be exposed at several places; this limestone contains layers of biotite and muscovite, which are parallel to the bedding planes of the rock that it enclosed. As there is little, if any, lime in the country rock, the calcite and lime silicates found in the mines are derived from a very limy bed of the sedimentary series, which is an explanation favored by Emmons, or the lime has been introduced along with the ore.

The Orebodies

The orebodies consist of lenses of heavy sulfide occurring in the Ocoee schists, and are somewhat similar in type to those found elsewhere in the Appalachians. The contacts of the orebody and the country rock appear to be roughly parallel to the bedding planes of the metamorphosed rocks. The lenses of ore have a general northeastward strike and a general dip to the southeast, though at places they dip northwest. The orebodies outcrop in three roughly parallel lines.

The primary ores are composed mainly of pyrrhotite, pyrite, calcopyrite and sphalerite, but the amount of pyrite varies considerably. The gangue material is quartz, calcite, tremolite, and numerous other silicates. Where the copper content is above 1½ per cent. or where there is a high sulfur content, the material is considered as ore. All of these ores contain a high percentage of iron and about 1½ per cent. zinc. Experiments have been carried on for a number of years by the companies operating in this district looking toward the recovery of the iron content of the ores. Recently the Ducktown Sulphur, Copper, & Iron Co. stated that it would put up a sintering plant for the recovery of this iron. Where the ore grades into lime silicate rock and the sulfides become less abundant, it is not commercially workable.

These ore zones vary from a few feet to nearly 200 ft. in width; the average width is probably between 50 and 75 ft. According to Gilbert, the ores from the different mines are more or less distinctive, pyrite being noticeably abundant at the Burra Burra

mine, while the Mary mine contains very little pyrite and tremolite is the chief gangue mineral. The ores from the London, Isabella, Eureka, and old Tennessee mines are much like the two types just mentioned, but are in general a mixture of the two, being intermediate between them.

On the School property, the ore has an approximate analysis of 1 per cent. copper, 29 per cent. sulfur, and 25 per cent. iron. This ore is slightly different from the ore mined and treated by the other companies in the district, and before it can be utilized a new process for its treatment must be developed if its mining is to be profitable. The Ocoee Mining Co.'s mine joins the old East Tennessee mine and its ore should be similar to the ore encountered there.

The Ducktown orebodies were originally capped by a heavy gossan, which was often 100 ft. thick and consisted of very pure iron ore (limonite). A large amount of this gossan, averaging 40 to 50 per cent. iron, has been shipped at different times as iron ore.

Below the gossan lies the zone of secondary sulfides, being the zone from which the "black copper" was obtained during the early days of this mining district. All of this black copper oxide has been mined out and it is doubtful if there are any places where it will be found in the future. This ore was remarkable for its fineness and its richness. Only an occasional small pocket of this ore can be found in the walls of some of the old workings. It is probable that this ore yielded from 20 to 30 per cent. copper, as the figures given by Currey[11] on some of the first ore shipped from this district show that it contained 14½ to 32½ per cent. copper. Henrich describes black copper oxide as follows: "The zone contained rich copper ores, distributed in patches of varying dimensions (but not as a continuous body) within a zone or layer extending more or less horizontally across the vein, in thickness varying from 2 to 8 ft., and more, above the sulfuret orebodies and below the gossan. Such a deposit would, at times, extend over the whole width of the orebody from wall to wall and for long distances along the strike. If of such horizontal extent, it was also usually of considerable depth. In other places, the black copper would be found only in small pockets or seams of limited extent and then usually along one or other of the walls of the ore deposit. Detached deposits of such ores would also occur more in the center of the ore deposit." The most important minerals of this "black copper" according to Gilbert was probably chalcocite.

There is a distinct relation between the bottom of the gossan deposit and the water tables of this region and, as would be expected, the top of the gossan roughly parallels the surface of the ground, except that it thickens on top of the high hills and is closest to the surface in the creek bottoms.

[11] *Op. cit.*, 74.

Notes on the Clinton Group in Alabama

By Truman H. Aldrich, M. E., Birmingham, Ala.

(Birmingham Meeting, October, 1924)

The red, or fossiliferous, ore is found in the Clinton group of the Silurian formation. This group is from 100 to 500 ft. thick in Alabama, and its outcrops have been mapped by the State or the U. S. Geological Survey. In some places, it is entirely missing (doubtless islands in the Silurian Sea). In Etowah County, in part of Greasy Cove and vicinity, the upper seam is a coral reef impregnated with the red ore; in this same county, step faults bring up the ore in three or four practically parallel ridges.

In Blount County and on Raccoon Mountain, the ore runs under the carboniferous rocks and outcrops in the valleys. When examining the logs of holes drilled for oil, wherever the drill has gone deep enough, the writer has found the Clinton group underlying the Warrior coal field. The following records of holes drilled primarily for oil, given in *Bull.* No. 22, Geological Survey of Alabama, show the presence of either ore or red rock, and suggest vast resources yet to be outlined and developed for ore in the future. The locations are given by number on the map.

Hole No. 1 was drilled 6 miles southeast of Russellville, Franklin County, by the Woodward Oil & Gas Co. It passed through 160 ft. of the Clinton, but only a small show of red ore was found at 1280–1400 ft.

A test well, No. 2, drilled near Atwood, Franklin County, in section 26, township 8, range 14, penetrated the Clinton at 1608 ft. and found 38 ft. of limy red rock, also 8 ft. of some blood red ending at 1820 ft., making 46 ft. of red rock in all. It is reported that some good ore was cut through but this work was done by a churn drill. At least 400 ft. of the formation was classified as Clinton.

Well No. 3, called Frankford Well, was bored by S. A. Hobson and associates in the northwest quarter of section 7, township 6, range 12, Franklin County. At 927 ft., it is supposed to have entered the Clinton; the log is as follows:

	Ft.
Sandy limestone with reddish, high ferruginous argillaceous inclusions	10
Same growing more ferruginous	18
Hematitic limestone	30
Same with slightly less iron	23
	81

ending at 998 ft. It is to be noted that the irony material occurs at the very base of the Clinton.

Hole No. 4, drilled near Bridgeport, Jackson County, encountered several hundred feet of Clinton, but the exact drill record is unknown, no ore was shown.

Several holes, No. 6, were drilled along the Brown's valley anticline in Jefferson County; the Clinton formation was penetrated in some, but no record is available.

The Pratt Consolidated Coal Co. made two tests with a diamond drill, one at Flat Creek, Jefferson County, in the northeast quarter of the northwest quarter of section 19, township 16, range 5 west, where the Clinton formation was penetrated at 2798 ft. The whole section showing the Clinton is given as it is the most important record preserved.

	Starting at 2798 Ft. Feet	Inches
Ferruginous sandstone, lean ore	0	6
Sandstone	30	6
Green shale, 2 ft. lean ore at top	4	6
Lean ore	0	3
Shale and sandstone	2	8
Lean ore	6	8
Sandstone	26	11
Green shale	6	3
Lean ore matter with white fossils	0	3
Green sandy shale	2	0
Lean sandy ore	0	6
Shale	1	3
Lean ore	0	3
Sandstones, limestones and shales interbedded	41	6
Iron ore	2	8
Coarse pink crystalline limestone with ore interbedded, shaly in places, ore about 50 per cent. rock	20	4
Ore, good fine grained (one piece ran 43.20)	7	2
Ore	0	1
Shale	0	4
Base of Clinton at	3003	

Good and lean ore is shown, which is highly significant; the best layer is at the base of the formation directly above the Trenton.

The second well, drilled at Praco, Jefferson County, about 3 miles southwest of the other was probably not finished down to the Trenton; it showed several layers of ore in the last 200 ft., one over 1 ft. thick. The two holes are much alike; this also is a diamond-drill hole. Considerable gas and some oil came out of this hole, and is still exuding.

Hole No. 7, or what is known as the Hamilton well, in Marion County, section 25, township 10, range 14 west, though 3 miles northeast of the town, was drilled by the Gulf Producing Co. At 2160 ft., a ferruginous

limestone 37 ft. thick was entered; immediately under is 2 ft. of hematic ore, which is underlaid with a ferruginous limestone 31 ft. thick. This is evidently an ore horizon.

Hole No. 8—the Pennsylvania Oil & Gas Co. drilled several wells in the vicinity of Jasper, Walker County. Well No. 1, in the northwest quarter of the southeast quarter of section 22, township 14, range 7 west, entered the Clinton horizon at 2610 ft. and continued through red material to 2720 ft., or 110 ft. of Clinton.

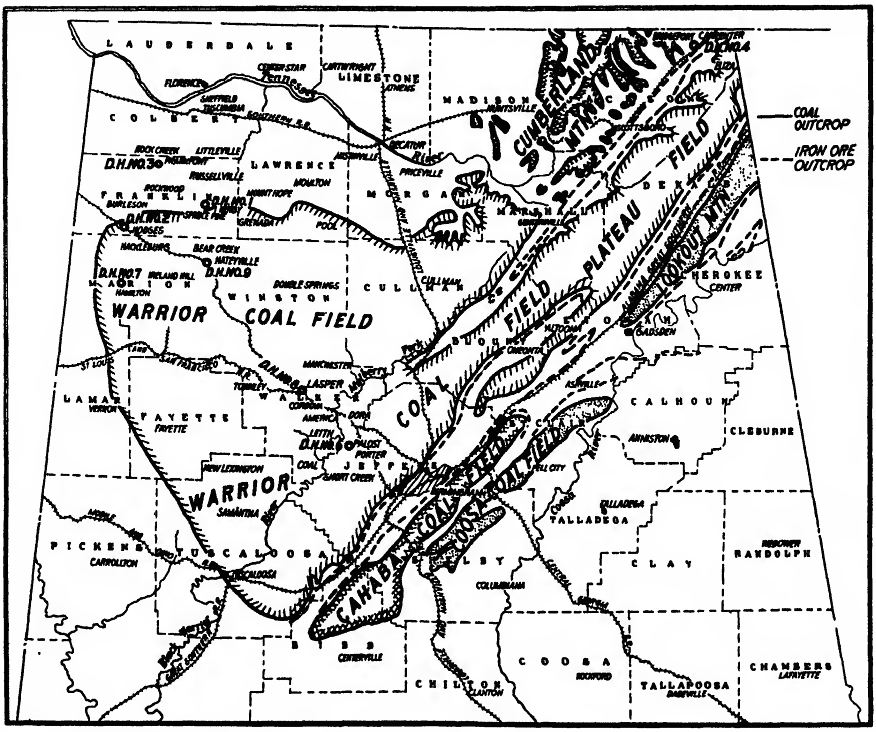

FIG. 1.—OUTLINE OF COAL FIELDS AND IRON-ORE OUTCROPS IN NORTHERN ALABAMA.

A well drilled at Calumet, 2.6 miles south of the other wells, penetrated red lime rock for 105 ft., or from 2675 to 2780 ft.

A well, No. 9, at Haleyville, Winston County, passed through 260 ft. of Clinton, basing at 2035 ft. The same company (Woodward Oil & Gas Co.) also drilled a well at Double Springs, almost in the center of the county, which passed through 150 ft. of Clinton. The records show red and green limestone and shale; the base is given as 1940 ft.

The outcrops of red ore are fairly well known and an enormous amount of available ore has not been touched. Of course the Birmingham valley deposits are exceptionally thick, but they vary in quality and quantity. It has been proved that the best ore runs in comparatively narrow bands

not parallel to the outcrops, perhaps, though following the shore lines of the ancient sea. The writer thinks that iron-producing bacteria may account for some deposits and the occurrence of a coral reef containing 24 to 30 per cent. of iron, even in "hard" ore, shows a deposition in a shallow sea, probably without replacement or chemical change. From the evidence adduced it is quite probable that the future supply is vastly greater than heretofore supposed.

The leaner ores have been successfully concentrated, but this whole question is being carefully studied by the Bureau of Mines Station at the State University, Tuscaloosa, with the State Geological Survey assisting.

As the Clinton formation underlies the Warrior coal field, it is reasonably certain that the red ore showing on both sides of Lookout Mountain and Raccoon Mountain must underlie these coal rocks; their dips confirm this.

Fig. 1 gives the outlines of the three coal basins and the approximate outcrops of the red ore; the small scale precludes great accuracy. We are indebted to the publications of the State Geological Survey for most of the information herein.

Phosphate Deposits of Idaho and Their Relation to the World Supply*

By Virgil R. D. Kirkham,† Moscow, Ida.

(New York Meeting, February, 1925)

North America has for many years led the world in phosphate production, but with development of African deposits and their marketing conditions with respect to European countries, this leadership will shortly pass to Africa. Algeria, Egypt, Tunis, and Morocco have large phosphate reserves and a correspondingly large production because of easy mining and a ready European market, which was developed during the war. An increase in home consumption is destined to develop for the eastern American fields, and the countries of the Pacific will provide a market for the western producers. New processes indicate a decrease in fertilizer costs, which will encourage a more widespread domestic use and assure better marketing conditions. The African deposits, although benefited by a water haul, have the disadvantage of being isolated from a source of acid so that the crude rock is shipped from Africa to its destination, whereas in the United States the chief product shipped is acidulated rock or various types of superphosphatic fertilizers. .

The principal types of phosphate deposits used in the manufacture of fertilizers are guanos, apatite, phosphatic marl, phosphatic limestone, phosphatic shale, and phosphate rock which is also known as phosphorite. Some of these deposits are found on each of the continents; Table 1 gives their occurrence, age, location, character, extent, etc. Most of the information found in this table represents a compilation of information published elsewhere in a different form and widely scattered.

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* Published by permission of Secretary of the Idaho Bureau of Mines and Geology.

† Assistant Professor of Geology, University of Idaho; Geologist of Idaho Bureau of Mines and Geology.

TABLE 1.—*Phosphate Deposits of the World*

Country	Occurrence	Geologic Age	Methods of Mining	Production	Reserves	Remarks
			Africa			
Algeria (Fr.)	Bedded deposits	Eocene	Open-cut and tunnel	8,950,000 long tons[3]	1,016,500,000 tons[1]	Continuation of Tunis, 58 to 68 % tricalcium phosphate
Egypt (Br. Prot.)	Bedded deposits in thin irregular beds	Cretaceous (?) Eocene	Open-cut and tunnel	885,000 long tons[3]	Extensive	Practically all of output is exported to Japan; contains 65 % tricalcium phosphate; production started in 1908.
Madagascar	Unknown	Unknown	Unknown	5,200 long tons[3]	Unknown	First production in 1922
Morocco (Fr.)	Bedded deposits	Pliocene Miocene Lower Eocene Cretaceous	Surface workings and tunnel	87,500 long tons[3]	1,000,000,000 tons[2]	70 km. from railroad; production started in 1921
Natal	Reefs and nodules of phosphate rock	Unknown	Unknown	None	Unknown	Near Weenen, Ladysmith, and Byrnetown
Senegal (Fr.)	Phosphate rock	Unknown	None	None	Unknown	At Dielor. Not workable
Tripoli (It.)	Bedded deposits	Eocene	Open cuts, and tunnel	None	Unknown	80 to 120 km. from city of Tripoli in beds over 1 m. thick; probably continuation of Tunis deposits
Tunis	Bedded deposits in lenses	Eocene	Chiefly shafts, tunnel and drift	25,480,000 long tons[3]	1,500,000,000 long tons[1]	Principal deposits in Gafsa field, southern half of country; phosphate exploited carries 58 % tricalcium phosphate; produces more phosphate than any foreign country; industry hampered by need of laborers
			Asia			
India	Nodules Apatite-mica pegmatites	Cretaceous	Shafts and tunnels	Left on dump	8,000,000 tons[3]	Unsuccessful

TABLE 1.—(*Continued*)

Country	Occurrence	Geologic Age	Methods of Mining	Production	Reserves	Remarks
Palestine (Jordan Valley).	Sedimentary phosphate rock (48 % tricalcium phosphate) Vein deposits (77 % tricalcium phosphate)	Unknown	Unknown	None	3,500,000 tons[4]	No shipments reported
Siberia (Uralsk and Turgai)	Low-grade phosphate rock (36 to 43 % tricalcium phosphate)	Unknown	Unknown	None	Uralsk 600,000,000 tons, Turgai 67,000,000 tons[4]	Undeveloped
			Australia			
New South Wales	Limestone caves, decomposed animal remains	Recent		7,600 long tons[3]	None	Local value only; exhausted in 1918
Queensland	Unknown	Unknown	Unknown	Unknown	400,000 tons[3]	
South Australia	Pockety deposits without stratification and of varying quality. Some is replacement of dolomitic limestone	Cambrian and pre-Cambrian limestones and dolomites	Quarry	50,000 long tons[3]	Unknown	55 to 70 % tricalcium phosphate
West Australia	Apatite veins and coprolite associated with chalk and ferruginous sand stones (Coastal islands also)	Unknown	Unknown	None	Unknown	Inaccessibility has prevented extensive production
Victoria	Phosphate rock	Unknown	Shaft and tunnel	11,200 long tons[3]	Unknown	
			Europe			
Belgium	Beds of phosphate nodules in a matrix of clay or in beds of phosphatic chalk (25 to 65 % tricalcium phosphate)	Upper Cretaceous to Lower Tertiary	Pit mining or stripping and tunnel	8,670,000 long tons[3]	Depleted	High-grade phosphate is exhausted and only low-grade remains. Import considerable high-grade phosphate and make superphosphate
England	Beds of phosphate nodules; coral remains and fossiliferous sandstone	Upper and lower greensand formation of Cretaceous Age Tertiary	Open cuts and tunnels	Less than 1,205,000 tons[5]	Limited	Output and deposits small; an importer of phosphate

Country	Occurrence	Geologic Age	Methods of Mining	Production	Reserves	Remarks
France	Phosphorite in fissures and pockets of residual and replacement origin in massive gray Jurassic limestone	Eocene	Pit mining and stripping	12,000,000 long tons[3] (approximate)	Depleted	High-grade deposits exhausted, only low-grade remaining.
Germany	Nodules Phosphorite deposits; dolomitic limestone in lens-like beds.	Cretaceous Devonian	Pit and underground workings	Unknown	Limited	Not producing at present; discovered in 1918; large tonnage of slag phosphate produced annually
Italy	Nodules	Unknown	Surface methods	Unknown	2,000,000 tons[6]	
Norway	Fluor-apatite in veins from magmatic segregation in gabbroic rocks	Unknown	Shafts and tunnels	151,500 long tons[5]	Limited	
Russia	Bedded sedimentary deposits carrying normally about 50 % tricalcium phosphate	Tertiary Cretaceous Jurassic Silurian	Underground workings	569,600 long tons[3]	1,500,000,000 tons[4]	Fields are divided into north, central, and southern; only latter is producing
Spain	Veins of apatite and phosphorite in crystalline and volcanic rocks (magmatic segregations)	Cutting sediments of Cambrian and Silurian age	Open cuts, pits and underground workings	695,000 long tons[3]	Limited	
Sweden	Apatite	Unknown	Open cuts and tunnels	18,600 long tons[3]	Limited	No production since 1912
Wales	Beds of nodules in association with crystalline limestone and shale	Lower Silurian	Tunnel and shaft		Limited	Production included with that of England
			North America			
Canada	Magmatic segregation of apatite from pyroxenite and pegmatite veins	(Lower Silurian?)	Quarrying chiefly, and some tunneling	358,000 long tons[7]	Medium	Practically abandoned deposits occur in Quebec and Ontario regions
United States				71,000,000 long tons	6,150,000,000 long tons[8]	Largest reserve in the world
Arkansas		Ordovician	Tunnels and shafts			Given in greater detail elsewhere

TABLE 1.—(*Continued*)

Name	Occurrence	Geologic Age	Methods of Mining	Production	Reserves	Remarks
Florida	Land pebbles	Pliocene	Hydraulic			
	Hard rock	Oligocene	Hydraulic			
	Phosphate					
South Carolina		Miocene				
Tennessee	Residual or blanket brown phosphate, white phosphate, blue phosphate	Ordovician Silurian Devonian	Open cut and tunnels			
Western Field	Bedded sedimentary deposits	Permian	Tunnels and open cut			
			South America			
Chile	Unknown	Unknown	None	None	Large	300 mi. north of Valparaiso, undeveloped
Dutch West Indies. (Is) off off coast of Venezuela—Aruba and Curacao	Phosphate rock 80 to 85 % tricalcium phosphate	Quaternary	Pit mining	585,000 long tons[3]	Limited	Mined and shipped to Europe (owned by English company); in 1913, mining was resumed after a suspension of 20 years
Salut and Connetables (Is) coast of French Guiana	Phosphate rock	Quaternary	Pit mining	48,800 long tons[3]	Approaching exhaustion	Worked by American company
Peru	Nodular phosphate rock	Unknown	None	None	Limited	Not used because of local preference for guano; guano output 150,000 long tons
			Islands of the Pacific Ocean			
Angour Is. in Pelew group east of Philippines	Rock phosphate	Quaternary	Surface workings	475,000 long tons[3]	2,000,000 to 4,000,000 tons of high grade rock[4]	Controlled by Japan; former German supply
Baker and Fanning Islands in Polynesia	Leaching from guano into limestone	Quaternary	Surface workings	Unknown	Unknown	
Christmas Is. (Br. in Indian Ocean)	Sea-bird leachings in limestone (80 % tricalcium phosphate)	Quaternary	Surface workings	2,586,000 long tons[3]	8,000,000 tons[5]	Shipped to Australia and Japan; deposits irregular but extensive and very high grade; British began to exploit in 1900

Name	Occurrence	Geologic Age	Methods of Mining	Production	Reserves	Remarks
Makatea Is. (Fr.) (Society Is. near Tahiti)	Irregularly distributed between reefs and pinnacles of dolomite	Quaternary	Surface—pick and shovel	550,000 long tons[3]	10,000,000 tons[4]	Shipped chiefly to New Zealand; some carries 85 % tricalcium phosphate
New Caledonia (Fr.) Huon Is.	Phosphate rock	Quaternary	Surface workings	10,000 long tons	Limited	62 % tricalcium phosphate
New Zealand.............	Beds 3 to 12 ft. thick in pockets of limestone	Miocene	Unknown	102,000 long tons[3]	Limited	
Ocean Is. (Br.) (Gilbert Archipelago. North of New Zealand)	Sea-bird leachings impregnating limestone forming deposits of phosphate rock many feet thick	Recent	Quarry—pick and shovel	2,876,000 long tons[3]	50,000,000 tons[9]	Among richest in the world
Pleasant Is. ((Nauru) Gilbert Archipelago)	Surface deposits between pinnacles of coral limestone	Recent	Quarry—pick and shovel	1,010,000 long tons[3]	90,000,000 tons[3]	Formerly owned by Germany. 180,000 tons to be delivered to England each year. 85 to 86 % tricalcium phosphate
Rasa Is. (Jp.) East of China	Phosphate rock (75 % tricalcium phosphate)	Quaternary	Surface workings	974,000 long tons[3]	3,000,000 tons[6]	Contains high percentage of aluminum and iron oxide; unsuitable for superphosphate; production includes several surrounding small islands
Tais Is. and West Carolina Is.	Leaching from guano into limestone	Recent	Surface workings	Unknown	Unknown	

[1] R. W. Stone: Phosphate in 1919. *American Fertilizer* (Mar. 12, 1921) **54**, No. 6.
[2] Strauss, L. Lloyd: Phosphate. *Eng. & Min. Jnl.-Pr.* (1922) **113**, 565.
[3] Yearly statistics of Imperial Mineral Resources Bureau of British Empire.
[4] R. W. Stone: Phosphate Rock: Political and Commercial Geology: J. E. Spurr, Ed., New York, 1920.
[5] R. W. Stone: Phosphate Rock. U. S. Geol. Surv. *Mineral Resources* (1918) Part II.
[6] Phosphates (1913–1919) Publication of the Imperial Mineral Resources Bureau of the British Empire, 1921.
[7] Yearly statistics of Canada, Dominion Bureau of Statistics.
[8] Yearly statistics of U. S. Geol. Surv. and Idaho Bur. of Mines and Geol.
[9] W. C. Phalen: The Conservation of Phosphate Rock in the United States. *Trans.* (1917) **57**, 99.

TABLE 2.—*Phosphate in the United States*

State	Occurrence	Geologic Age	Methods of Mining	Production	Reserves	Remarks
Alabama	Brown phosphate similar to that in Tennessee	Ordovician	Surface methods	None	Unknown	Inferior to Tennessee phosphate; little likelihood of any development in this field in near future
Arkansas	Original sedimentary deposit analogous to the blue phosphate of Tennessee, but in Cason shale	Ordovician	Surface methods and drifts	A small production included with Tennessee	20,000,000 tons[1]	Quality is inferior to Tennessee and Florida phosphates; little activity; unadapted to manufacture of acid phosphate; field well situated for demand west of Mississippi River
Florida	Hard rock (pebbles and boulders embedded in matrix of fine material) Plate rock (formed through disintegration of boulders Land pebble (in sand and gravel) River pebble Soft phosphate (in matrix of hard rock and land pebble deposits) Phosphatic marl	Oligocene (Miocene?) Pliocene Pleistocene Recent	Open-pit, stripping of overburden, excavating, washing, sorting, drying Hydraulic methods largely used in land-pebble mines	43,034,033 long tons[2]	227,000,000 long tons[1]	Leading state in production of phosphate; hard rock and land-pebble types only are mined to any extent; conveniently located for shipment by rail or water to other parts of U. S. or abroad; production began in 1888
Georgia	Phosphatic marls and low-grade phosphatic deposits	Cretaceous Tertiary	Surface methods	None	Limited	Not of commercial importance
Idaho	Bedded oolitic sedimentary deposits; brown, gray, and black rock	Permian (Phosphoria)	Surface stripping tunnels and drifts	205,000 long tons[2]	5,500,000,000 long tons[3]	Largest reserve of phosphate in world; development hindered by distance from markets and high freight rates
Kentucky	Residual deposits from phosphatic limestones	Ordovician	Quarry	A small production included with Tennessee	1,000,000 tons[1]	Mined at one place only; quality lower than Tennessee deposits; as distributing point for middle west, Kentucky is better situated than Tennessee

Montana................	Bedded oolitic sedimentary deposits	Quadrant formation (Permian, Upper Pennsylvanian)	Undeveloped	None	180,000,000 long tons[1]	Deposits easily accessible to railroads, in close proximity to smelting plants where sulfurous fumes are available for manufacture of sulfuric acid and acid phosphates
North Carolina...........	Marls, phosphate beds in pockets on small streams a few hundred feet downstream from the marl beds	Cretaceous and Tertiary	Surface stripping	Unknown; probably small. Local use only	Limited	Not counted among phosphate producing states; worked in 80's and early 90's; rock inferior to that of South Carolina and more difficult to mine
South Carolina...........	Land rock (bed of irregularly phosphatised marl) River rock (rounded fragments in river bottoms and banks)	Eocene Oligocene Miocene Pliocene Pleistocene Recent	Dredges and steam shovels	13,343,238 long tons[2]	9,000,000 tons[1]	Land rock only mined since 1910; field has apparently passed period of maximum production; industry began in 1868; chief producer until advent Florida and Tennessee
Tennessee................	Brown rock (residual deposit left by leaching of phosphate limestone) Blue Rock (bedded phosphate unchanged) White rock secondary origin, more recent than the Silurian and Devonian deposits. Cavern formed	Ordovician Devonian and Mississippian	Open-cut for most of brown phosphate. Tunneling for most of blue and white rock	11,187,500 long tons[2] (Total includes a small production from Kentucky)	88,000,000 tons[1]	Deposits rank next to those of Florida; brown phosphate is most important commercially; first phosphate marketed in 1893
Utah....................	Phosphatic shales	Permian (Park City or Phosphoria formation) Mississippian (Brazer limestone)	Tunnels and drifts	Small	96,750,000 tons[1]	Deposits are generally remote from railroads; fields not sudied in great detail; reserves probably larger than given
Wyoming................	Occurrence same as Idaho phosphate	Permian (Park City or Embar), equivalent of Idaho phosphate	Tunnels and drifts	Small	37,200,000 tons[1]	Wyoming phosphate inferior to Idaho phosphate; total reserves probably greater than given

[1] G. R. Mansfield: Phosphate Resources of the United States; Second Pan-American Sci. Con. *Bull.* (1915–16) 21.
[2] Compilation of yearly statistics of the U. S. Geol. Surv. *Mineral Resources.*
[3] Estimates of U. S. Geol. Surv. and Idaho Bureau of Mines and Geology.

This country has a variety of phosphate deposits. Many of them are of low phosphate content and will remain undeveloped for a long time. Curiously, the region that, by its agricultural age, first needed phosphate in the form of fertilizer was that in which the first commercial deposits of phosphate rock were found. This nearness of market to source created an industry that has flourished for more than 60 years. Many foreign countries have used phosphate fertilizers for a much longer period and, consequently, have used all their high-grade deposits and much of their low-grade material. This country, although having used much of its eastern supply, retains so much untouched high-grade rock in the Western States, as to put off the use of the equally large low-grade deposits to a far distant date.

The demand for fertilizer in European countries and in the South Atlantic and Mississippi Valley States, which have been cropped for several generations, has developed a fertilizer industry in excess of $125,000,000 a year. More than 71,000,000 long tons of high-grade phosphate rock have been mined; the average annual production for 10 years is about 2,500,000 tons, though 4,104,000 tons were produced in 1920.

Although Europe is not now taking as much American phosphate as before the war, the industry is assured of a steady increase because of the increased domestic consumption produced by an awakening of American agriculturists to their needs and because of the new field for western phosphates in oriental countries.

Table 2 shows the position of the various states in regard to production, reserves, etc., but does not include the names of states in which are found deposits of apatite, nelsonite, and low-grade marl, which have no commercial importance now and which give no evidence of importance in the near future.

Idaho Phosphate Deposits

The Idaho phosphate field, the largest within the United States, and so far as known the largest in the world, lies in the southeastern corner of the state. Phosphate lands have been examined in detail by the U. S. Geological Survey in Bannock, Bingham, Bonneville, Bear Lake, Caribou, Madison and Teton Counties and an area of 1800 sq. mi. is believed to be underlain, at a minable depth, by commercial phosphate rock. The most accessible part of the field lies in Bear Lake and Caribou Counties, and is served by the Oregon Short Line of the Union Pacific System. Branch railways serve some of the districts and wagon hauls of from 1 to 12 miles connect many properties with the main line. Probably 95 per cent. of the deposit is untouched because of lack of cheap transporta-

tion, but favorable grades along drainage lines assure for the future many branch lines and spurs.

The topography of southeastern Idaho is rough. The region is made up of a great series of tilted, folded, and deformed sedimentary rocks that in places have been cut by great overthrust and normal faults. The maximum relief in the area is more than 4000 ft. and many points exceed 9800 ft. in altitude. Several large rivers, lakes, basins, and ranges are found in the area, the most important of which are Snake and Bear Rivers; Bear and Grays Lakes; Teton Basin and Star Valley; and the Preuss, Aspen, and Caribou ranges.

Geology of Idaho Deposits

The rocks are mainly sedimentary with a rather full stratigraphic range from Lower Cambrian to Quaternary. This stratigraphic series includes more than 40,000 ft. of sediments and sixteen unconformities. The series includes forty-eight formations distributed from the top of the section to the bottom, as follows: Alluvium of two ages, travertine, basalt, quartz-latite, and rhyolite in the Quaternary; basalt, dacite, rhyolite, trachyte, andesite, volcanic ash, the Salt Lake formation and the Wasatch formation in the Tertiary; the Wayan formation, Tygee sandstone, Draney limestone, Bechler formation, Peterson limestone, and the Ephraim formation in the Cretaceous; the Stump and Preuss formations, Twin Creek limestone, and Nugget sandstone in the Jurassic; the Wood shale, Deadman limestone, Higham grit, Timothy sandstone, Thaynes group and Woodside shale in the Triassic; the Phosphoria formation which is the phosphate-bearing series in the Permian; the Wells formation in the Pennsylvanian; the Brazer and Madison limestones in the Mississippian; the Three Forks and Jefferson limestones in the Devonian; the Laketown dolomite, in the Silurian; the Fishhaven dolomite, Swan Peak quartzite and Garden City limestone in the Ordovician; the St. Charles, Nounan, Bloomington, Blacksmith, Ute, Spence, and Langston formations, and the Brigham quartzite in the Cambrian period.

The region is greatly folded into wide synclinoria and narrow complementary anticlinoria. Many of these folds range between 30 to 50 miles in length and show a notable parallelism. The more important faults are overthrust in character and include certain ones with tremendous length and displacement. Normal faults of considerable size are abundant. Both faults and folds have a distinct economic relation to the phosphate beds, inasmuch as they have revealed the Phosphoria formation in many places where otherwise it would be buried under a vast thickness of overlying beds; in other places they have brought it close enough to the surface to be minable.

The area is made up of a series of thrust-fault blocks separated by extensive overthrust faults running in a northerly and southerly direction.

The thrust in each instance is from west to east, thus bringing older rocks on the west of each fault into a position overlying younger rocks on the east. In these blocks, between the faults, are found synclinoria and anticlinoria, the folds of which are approximately parallel to one another and to the fault lines. Many of these folds are fairly regular in form but the

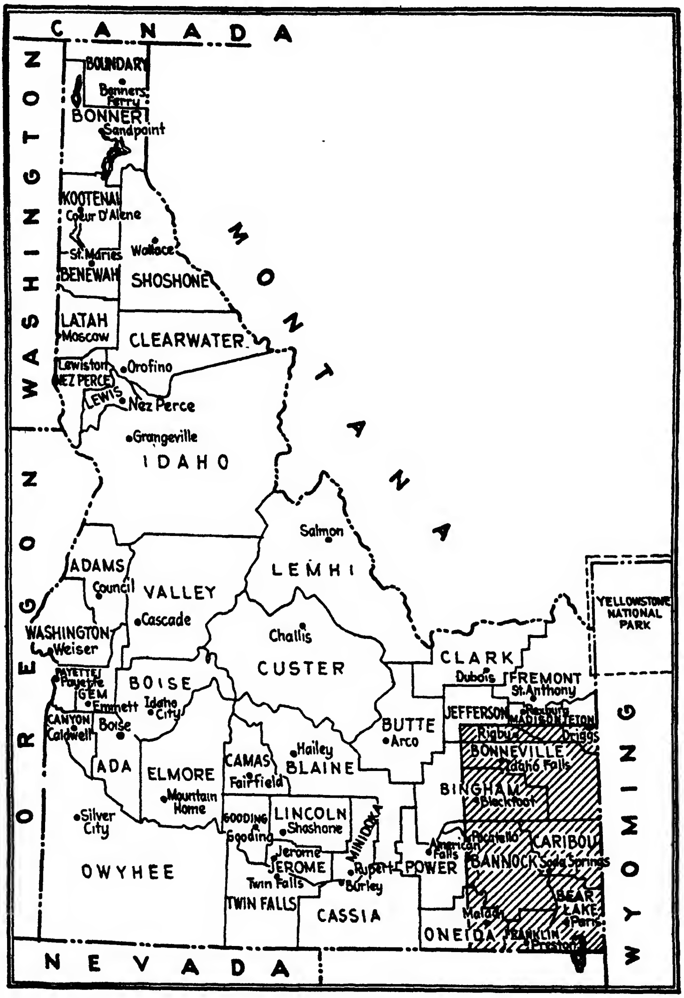

Fig. 1.—Location of phosphate fields of Idaho.

greater number are unsymmetrical or overturned. The folding is so intense that fifty folds have been mapped and named. Among the many important overthrust faults along which phosphate is exposed are the Bannock overthrust, 270 miles long with a horizontal displacement of 35 miles, and the Absaroka overthrust, 200 miles long with a horizontal

displacement of 25 miles, and a stratigraphic throw of 20,000 ft. The St. John fault and the Snake River fault are overthrusts with a length over 35 miles and are similar to the larger overthrusts except in the degree of displacement. The Darby overthrust is credited with a length of 125

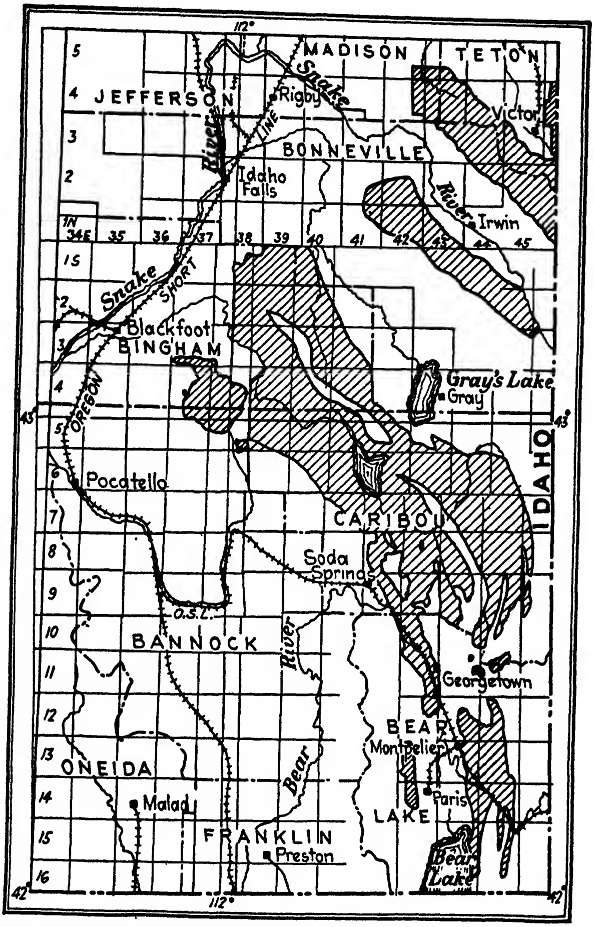

FIG. 2.—SHADED AREA IN FIG. 1; SHADED AREA HERE SHOWS LAND UNDERLAIN BY PHOSPHATE ROCK.

miles and a horizontal displacement of more than 15 miles. The Putnam overthrust represents the smallest and lies in the northwestern part of the region. The importance of faulting is attested by the number that have been mapped and named; more than sixty reverse and normal faults have been studied. Many curious and unusual structures result from this intense folding and faulting; horsts and grabens, fan folds, drag folds, and "swallowtail" folds are often found. In general, the whole structural scheme is somewhat similar to that of the southern Appa-

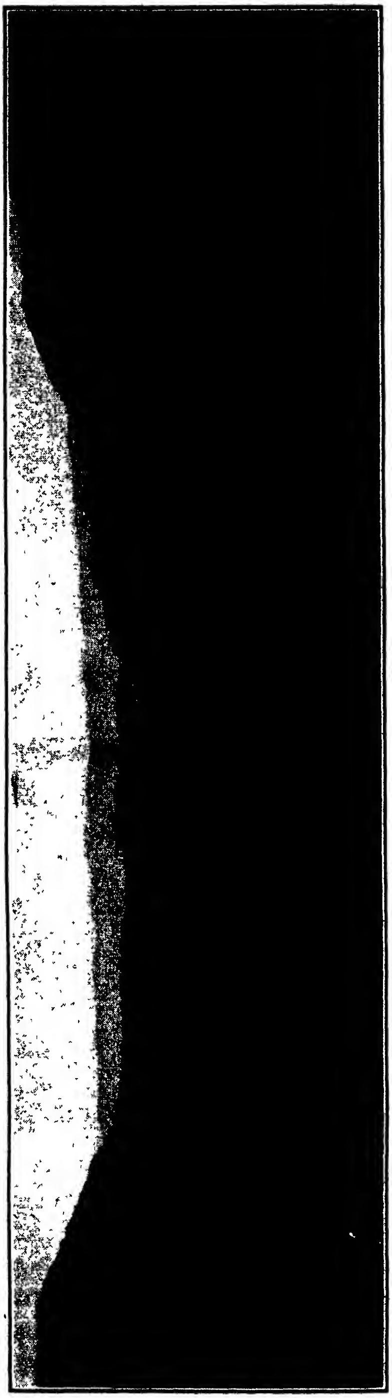

Fig. 3.—Typical terrane of southeastern Idaho, showing several physiographic cycles and rock terraces.

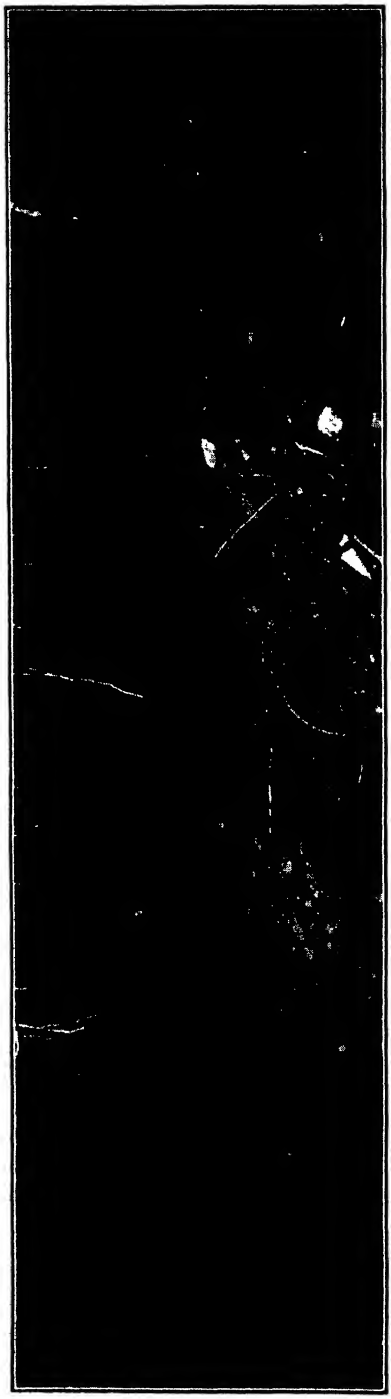

Fig. 4.—Open cut, showing phosphate beds in Georgetown Canyon.

lachians, according to Dr. F. B. Laney. The phosphate is preserved in the synclines, in the overthrust block of the Bannock and other faults, where the Carboniferous sediments have been brought to the surface and eroded.

Idaho rock phosphate is characterized by a marked oolitic texture. Rounded concentric particles ranging in size from minute bodies, visible only by aid of a lens, to pebbles more than ½ in. in diameter, make up their texture. The brown and gray rock are easily confused with coarse sandstones. The color of this rock phosphate varies from a jet black as in the Montpelier area and an iron-stained brown at Paris and St. Charles, to a dull gray near Georgetown. The weathered outcrop is generally a characteristic bluish-gray color.

The rock and the associated phosphatic shales and limestones give off a peculiar fetid odor when broken, which is typical of the phosphate-bearing strata and aids in identifying it in the field. The odor is no indicator of the richness of the deposits and disappears when the rock is heated. The rock in the workable seams carries from 32 to 40 per cent. of phosphoric acid and has a specific gravity ranging from about 2.90 to 2.95. A specimen of phosphate rock from 8 miles east of Georgetown, Idaho, gives the following analysis.[1]

Analysis of Phosphate Rock from Near Georgetown, Idaho

	Per Cent.		Per Cent.
Insoluble	2.62	TiO_2	None
SiO_2	0.46	CO_2	2.42
Al_2O_3	0.97	P_2O_5	33.61
Fe_2O_3	0.40	SO_3	2.16
MgO	0.35	F	0.40
CaO	48.91	Cl	Trace
Na_2O	0.97	Organic Matter	Not det.
K_2O	0.34		
H_2O	1.02		95.97
H_2O+	1.34		

Origin of the Deposits

The origin of these deposits has received much attention and has great economic importance, especially in computing reserves. If the rock is of secondary origin only shallow deposits of high-grade rock could be expected to underlie these areas. A great amount of detailed work by many competent geologists has revealed that, to the contrary, they may be considered as true bedded deposits, laid down under marine conditions similar to shale or limestone. The apparent great extent and uniform

[1] H. S. Gale and R. W. Richards: Preliminary Report on Phosphate Deposits in Southeastern Idaho and Adjacent Parts of Wyoming and Utah. U. S. Geol. Surv. *Bull.* (1909) 430, 465.

thickness cause them to be regarded as true sedimentary strata. Estimates as to reserve are made upon this assumption.

The sources of the phosphoric acid and the mechanics of its accumulation have been the cause of considerable controversy. An abstract of Blackwelder's[2] hypothesis as to origin is substantially as follows.

FIG. 5.—BLACK PHOSPHATE BED OPENED BY SURFACE STRIPPING AT WATERLOO MINE.

In the ocean special conditions of currents, temperature, etc., not yet understood, may have induced wholesale killing of animals over large areas and accumulation of putrefying matter on the sea floor in moderate and shallow depths. Decomposition through the agency of bacteria produced ammoniacal solutions which dissolved the solid calcium phosphate in bones, teeth, brachiopod shells, and tissues. For physicochemical reasons, already partly understood, the phosphatic material was quickly redeposited in the form of hydrous calcium carbo-phosphates, locally filling, incrusting, and replacing shells, teeth, bones, etc., but especially forming small rounded granules of colophanite and finally a phosphatic cement among all particles. After having been formed in quiet water, some of the granules were reached by bottom-scouring currents and incorporated in clastic deposits and in some instances were strewn over eroded rock surfaces and so became constituents of basal conglomerates.

Some of Mansfield's[3] conclusions in regard to the origin are as follows:

1. The phosphatic oolites and their matrix were probably deposited originally as carbonate of lime in the form of aragonite.

2. The waters were probably shoal and of warm or moderate rather than of cold temperature.

[2] Eliot, Blackwelder: Origin of Rocky Mountain Phosphate Deposits: *Bull.* Geol. Soc. Amer. (1915) **26**, 100.

[3] G. E. Mansfield: Origin of the Western Phosphates of the United States. *Am. Jnl. of Sci.* (1918) **46**.

3. The phosphatization of the oolitic deposit was probably subsequent to its deposition rather than coincident with it, . . . under conditions favorable for the deposition of the carbonate but not of the phosphate of lime.

4. Cooler temperature in the waters of deposition, checked the activities of the denitrifying bacteria and hence the conditions favorable for the formation of oolitic limestone. At the same time plant and animal life increased in the waters and furnished the decaying matter necessary for the phosphatization of the oolitic limestone in the general manner set forth in Blackwelder's account given above. Perhaps Pardee's idea of glacial climate may have a bearing in this connection.

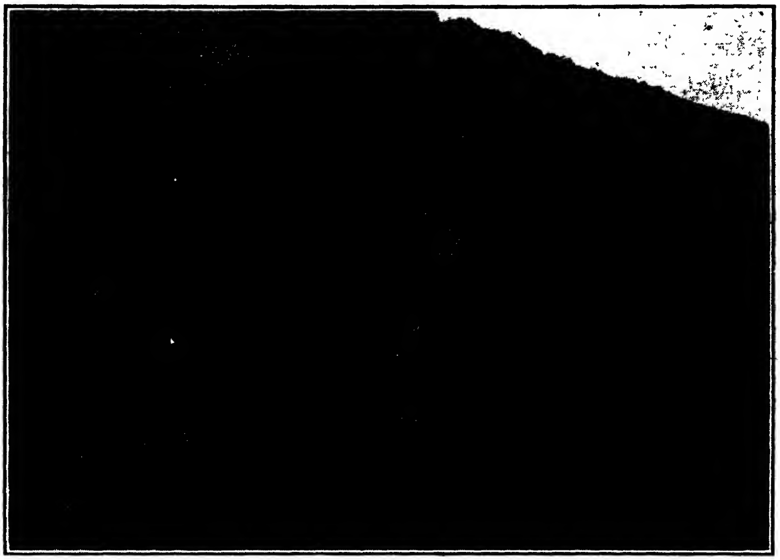

FIG. 6.—SURFACE WORKING; THIS AND FIG. 5 SHOW INCLINATION OF BEDS ALONG DIP SLOPE.

5. The sea in which the phosphate was deposited was closed off on the east, south, and west, but may have had connections with the ocean northward and northwestward, for Girty[4] notes faunal resemblances traceable into Alaska, Asia, and eastern Europe, and Adams and Dick[5] report the discovery of phosphate at apparently the same horizon in Alberta.

METHODS OF MINING

Early mining consisted chiefly of surface stripping and open cuts, where the overburden was no more than 20 ft. thick. Present development consists of entering the flanks of the synclines, anticlines, or monoclines by adits at the lowest possible surface levels. On encountering the beds, drifts are driven along the strike of the phosphate. From the

[4] G. H. Girty: The Fauna of the Phosphate Beds of the Park City Formation in Idaho, Wyoming and Utah; U. S. Geol. Surv. *Bull.* 436 (1910) 8.

[5] F. D. Adams and W. J. Dick: Discovery of Phosphate of Lime in the Rocky Mountains, Commission of Conservation, Canada, Ottawa (1915).

drifts, stopes are raised to the surface on the dip slope of the phosphate bed. The adits and drifts are the haulageways, and these and some of the stopes act as the airways. Easy mining by this method requires steeply dipping phosphate beds in order that gravity may carry the ore from the stopes to the drifts.

Economic Factors

The western phosphate deposits, although as yet little utilized, are being used chiefly in the manufacture of superphosphates for fertilizer.

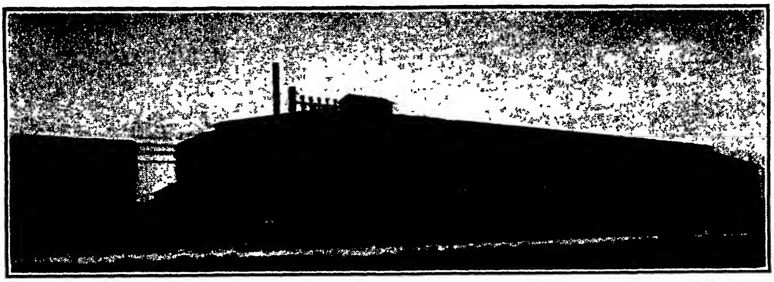

Fig. 7.—Sulfuric-acid plant of Anaconda Copper Mining Co., at Anaconda, Mont.

The companies now mining phosphate and manufacturing superphosphates are meeting the demand for fertilizer from the Pacific Coast States.

Fig. 8.—Superphosphate plant of Anaconda Copper Mining Co., at Anaconda, Mont.

Numerous processes for making soluble phosphates have been developed and described.[6]

[6] H. S. Gale: Suggested Manufacture of High-grade Superphosphates. U. S. Geol. Surv. *Bull.* 470 (1910) 449.

W. C. Phalen: Phosphate Rock. U. S. Geol. Surv. *Min. Res.* (1915) II, 239.

W. H. Waggaman and W. H. Fry: Phosphate Rock and Methods Proposed for its Utilisation as a Fertilizer. U. S. Dept. Agr. *Bull.* 312 (1915).

SUPERPHOSPHATE OR DOUBLE PHOSPHATE

Because of its relatively low phosphoric acid content, shipping ordinary acid phosphate over long distances is uneconomical. Superphosphate, or "double phosphate," a product containing from 48 to 50 per cent. available phosphoric acid, is made for long-distance shipment.

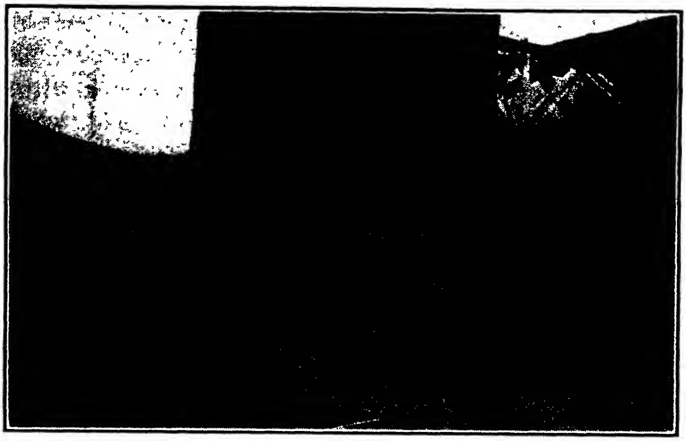

FIG. 9.—TRUCKING PHOSPHATE ROCK FROM MINE BINS TO RAILROAD.

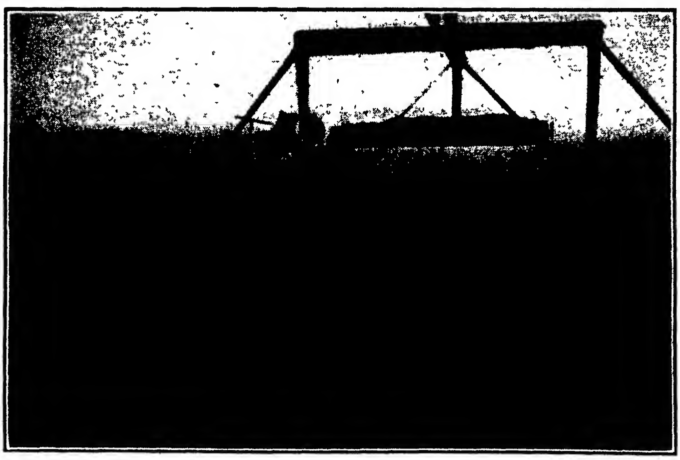

FIG. 10.—TIPPLE LOADING OF CARS AT MONTPELIER, IDA.

In the manufacture of superphosphate, the phosphate rock is treated with sulfuric acid, producing phosphoric acid, which is filtered, concentrated by evaporation, and used to treat additional phosphate rock. The resulting mix is known as "superphosphate" or "double phosphate." The raw phosphate rock is crushed, dried, and ground in ball-mills to pass through a 65-mesh screen, and then digested with 60° Bé. sulfuric

acid in air agitators. The pulp is washed and filtered, while the liquid is concentrated, by evaporation, to 65 per cent. H_3PO_4. This concentrated phosphoric acid is used to treat fine raw phosphate rock in the mixers. The mixed material is discharged into "dens," and then conveyed to the driers. After being dried and disintegrated, it is bagged ready for shipment. The chemical reactions are:

$$Ca_3(PO_4)_2 3H_2SO_4 + 6H_2O \rightarrow 2H_3PO_4 + 3(CaSO_4.2H_2O)$$
$$4H_3PO_4 + Ca_3(PO_4)_2 \rightarrow 3CaH_4(PO_4)_2.$$

Treble superphosphate is made by treating raw rock with an equal weight of 60 per cent. H_2SO_4 to make phosphoric acid, which is then mixed with pulverized raw rock in the proportion of two parts of phos-

FIG. 11.—PHOSPHATE BUNKERS AND LOADING MACHINERY AT MUNICIPAL TERMINAL No. 4, PORTLAND, ORE.

phoric acid to three of raw rock. This product contains more than 48 per cent. of available phosphoric acid.

PROCESSES IN WHICH PHOSPHOROUS OR PHOSPHORIC ACID IS VOLATILIZED

Although the various processes for the production of available phosphoric acid from phosphate rock by volatilization are still in the experimental or semicommercial stage, they show such promise of being commercially practicable and appear so well suited for the utilization of the Idaho phosphates that they are well worth considering here.

Most of the work on the volatilization processes has been done by the Bureau of Soils of the U. S. Department of Agriculture. Ross, Carothers, and Mery[7] did the first work on electric-furnace volatilization of phosphoric acid at Arlington Farm, Va. It was found that concentrated phosphoric acid could be so made that additional cost of manufacture would be offset by the saving in freight. They showed that with electric power at $25 per horsepower-year, phosphoric acid (P_2O_5) could be pro-

[7] W. H. Ross, J. N. Carothers and A. R. Mery: Use of Cottrell Process to Recover Phosphoric Acid Evolved in Volatilization Method of Treating Phosphate Rock: *Ind. & Eng. Chem.* (1917) 9, 26.

duced and recovered at a cost of 3.37 cents per pound exclusive of interest on investment, taxes, and royalties. This cost compared very favorably with that of the H_2SO_4 method. Later, Waggaman and Wagner showed that the mine-run phosphates of Florida, which in their natural state contain impurities that preclude that treatment with sulfuric acid until after thorough washing and screening, could be smelted directly in the electric furnace. Further work was done by Waggaman and Turley, using an oil-fired funace.

The best test of a series showed a volatilization of 97 per cent. of the phosphoric acid in the charge, with a yield of 5.56 lb. P_2O_5 per gallon of fuel oil costing 5 cents per gallon. The cost of the fuel constituted 14.4

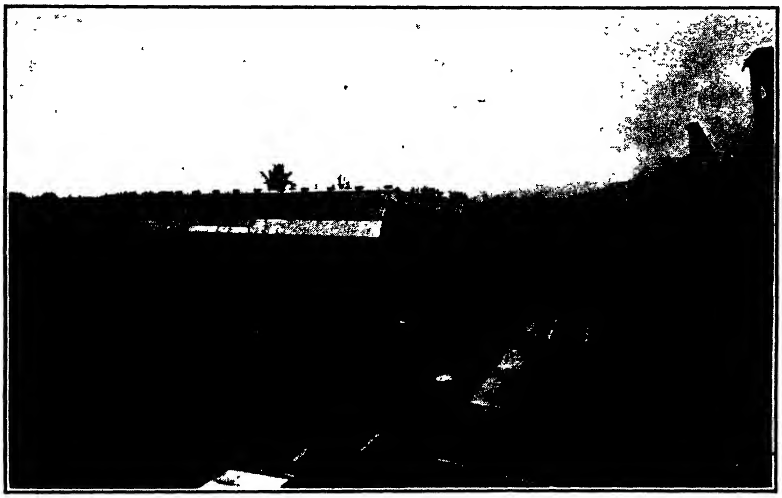

Fig. 12.—Another view of phosphate bunkers at Portland, Ore.

per cent. of the value of the products for fertilizer purposes; while in the sulfuric acid process the cost of H_2SO_4 is 23 per cent. of the value of the products. The phosphate rock used was run-of-mine material from the hard-rock phosphate mines near Newberry, Fla.

The production costs per ton of phosphoric acid by the volatilization method are much lower than the costs by the sulfuric-acid process, as shown by the figures of $49.83 for the former and $81.25 for the latter. This makes the cost per pound of P_2O_5 at 2.49 cents by the volatilization method and 4.05 cents by the acid process.

Recently, some work has been done using coal dust as a fuel in the volatilization of the phosphoric acid. Compressed air is used to blow the coal dust into the furnace and to supply the air necessary for the combustion of the fuel and the oxidation of the phosphorus. Indications are that the coal-dust fired furnace can be successfully applied here.

Some of the advantages of the volatilization process are:

1. Low-grade phosphates can be treated by this process; these could not be treated by the sulfuric acid process; many of the low-grade phosphates are almost self-fluxing.
2. Elimination of concentration by washing is effected.
3. A high-grade product suitable for long-distance shipping is obtained.
4. The cost of production per unit of phosphoric acid is cheaper than by the acid process.

Typical Plants Using Idaho Phosphate Rock

The Mountain Copper Co., Ltd., Martinez, Contra Costa County, Calif., manufactures acid phosphate called "Superphosphate" containing 17.50 per cent. available P_2O_5. Its flow sheet is as follows:

Flow Sheet

Idaho phosphate rock (70–85 per cent. Ca_3PO_4)
Stock piles
↓
Bunker
↓
Jawcrusher
↓ ↓
Kent mills
↓
Newago screens
↓ ↓
H_2SO_4 Undersize Oversize
↓ ↓
Mixing chambers
↓
Den (12 hours)
↓
Disintegrating knives
↓
Conveyor
↓
Piles.

The shipments of rock are received from Idaho and unloaded into stock piles from which the rock is moved to a bunker that discharges, through a jaw crusher, into Kent mills, which deliver through Newaygo screens into the "flour" bin.

From the flour bin, the ground rock is delivered into a mixing bowl in batches of about 600 lb.; sulfuric acid is delivered into this bowl simultaneously with the "flour." Enough sulfuric acid is added to satisfy two

of the three molecules of lime contained in the tricalcium phosphate; this leaves the third lime molecule in combination with the phosphoric acid as monobasic or "water soluble" phosphoric acid. After the charge is thoroughly mixed, it is dropped into a brick silo, or den where, it remains

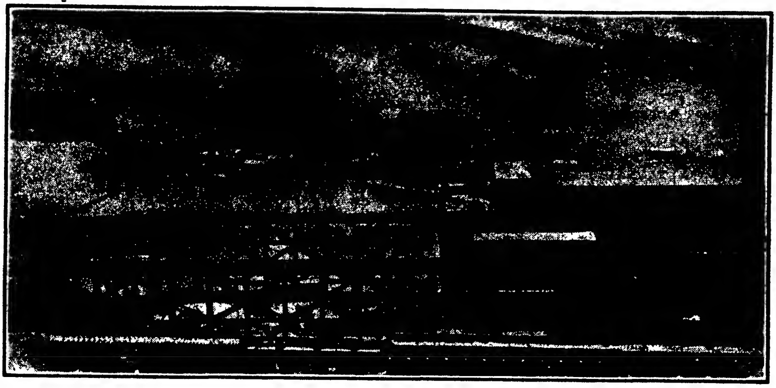

FIG. 13.—TRACK, BINS, AND PART OF PHOSPHATE MINES OF ANACONDA COPPER MINING CO., AT CONDA, IDA.; PART OF TOWN LIES IN CENTER OF PICTURE.

overnight, after which it has reacted and set sufficiently for it to be discharged through disintegrating knives on to a conveyor. The conveyor carries the material to the storage piles, where it cures for several weeks before shipping.

FIG. 14.—PLANT OF IDAHO PHOSPHATE CO. (SUCCESSOR TO THE WESTERN PHOSPHATE CO.), PARIS, IDA.

The acid phosphate produced, called "superphosphate," is guaranteed to contain 17.5 per cent. available phosphoric acid; it usually contains 16.75 per cent. monoflasic, 1.00 per cent. dibasic, and 0.50 per cent. tribasic phosphoric acid.

The Anaconda Copper Mining Co., Anaconda, Mont. manufactures "superphosphate" or "double phosphate" containing 48 to 50 per cent. available P_2O_5. Its flow sheet is as follows:

Flow Sheet

Idaho phosphate rock in cars (70–85 per cent. Ca_3PO_4)

Bins
↓
Blake crusher (1½-in. opening)
↓
Storage bin
↓
Ruggles Coles rotary drier
↓
Hardinge ball ↓ mill
↓
Newaygo screen (80-mesh)
↓
Undersize — Oversize (returned to Hardinge ball mill)
↓
Storage bin
↓
60° Bé. H_2SO_4 300 cu. ft. bin — No. 2 Dorr thickener overflow weak H_3PO_4
↓
No. 1 agitator
↓
overflow
↓
No. 2 agitator
↓
overflow
↓
No. 3 agitator
↓
overflow
↓
No. 1 Dorr thickener
↓
overflow — Underflow — No. 3 Dorr overflow

overflow
↓
(22 – 25 per cent. H_3PO_4)
↓
Tower evaporator
↓
Strong H_3PO_4 (50° Bé).
↓
80-mesh phosphate rock
Rock → Pratt mixer
↓
Dens
↓
36-in. belt
↓
Disintegrating knives
↓
Ruggles Cole drier
↓
Ground in Sturtevant ring role mill
↓
Sacked.

Underflow ↓ No. 3 Dorr overflow ↓
No. 2 Dorr thickener
↓ Overflow
↓ Storage tank
↓ No. 1 agitator

No. 2 Dorr thickener
↓ Underflow
↓ No. 3 Dorr thickener
↓ Overflow → No. 2 Dorr thickener → No. 1 agitator Above
↓ Underflow → Oliver filter
Oliver filter → Filtrate and wash → No. 3 Dorr thickener
Oliver filter → Cake → Waste

All incoming rock is dried and ground to pass through an 80-mesh screen, and then discharged into a storage bin. From the bin, it goes through a series of Dorr agitators. Sulfuric acid is added to the first agitator along with the fine rock. This produces weak phosphoric acid, which is removed in subsequent Dorr thickeners and elevated to a tower evaporator. The phosphoric acid is concentrated from 22° to 50° Bé. (65 per cent.) in the coal-fired evaporator. This strong acid is mixed with fresh finely ground rock and then goes to the dens. It is then disintegrated, dried, ground, and shipped as "superphosphate" containing 48 to 50 per cent. available phosphoric acid in the form of $CaH_4(PO_4)_2$.

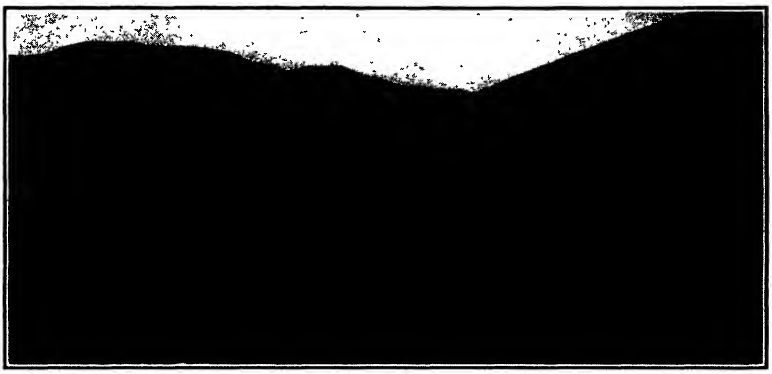

FIG. 15.—WATERLOO MINE OF SAN FRANCISCO CHEMICAL CO., AT MONTPELIER, IDA.

As most of the phosphate fertilizers are used in the Eastern and Central States, the future utilization of the Idaho phosphates lies in their conversion into products high in available phosphoric acid, to offset the high freight rates in order to compete with eastern phosphoric-acid fertilizer. The processes most suited are those for the conversion of the phosphate rock into acid phosphate, and superphosphate or double phosphate by sulfuric-acid methods, and into concentrated phosphoric acid by the volatilization method. The acid phosphate can stand shipment charges to the Western States. The superphosphate and concentrated phosphoric acid can be shipped to all parts of the country.

With improvement in methods and with modification of the furnace for coal-dust firing, the volatilization method for the production of phosphoric acid seems to be well suited for the treatment of the Idaho phosphates. The coal beds in Teton County are located on the northern edge of the phosphate area and may be adapted for coal-dust firing. With the possibility of oil in southeastern Idaho and western Wyoming, oil-fired furnaces might be applicable. By combination of the strong phosphoric acid with nitrogen and potassium salts, a high-grade fertilizer can be produced that will stand shipment to all parts of the United States and to foreign countries.

Obstacles in Marketing

The Idaho deposits have, as their greatest disadvantages, a freight rate schedule that will not permit competition with the Tennessee deposits in the Mississippi basin or east of it; and which is equally prohibitive in an attempt at competition with the operators of guano deposits on the islands of the Pacific in supplying the Pacific Coast States and countries bordering the Pacific. However, the island deposits have relatively small reserves and are rapidly nearing depletion. Portland, Ore., has prepared for the incipient great phosphate trade of Idaho with the Orient

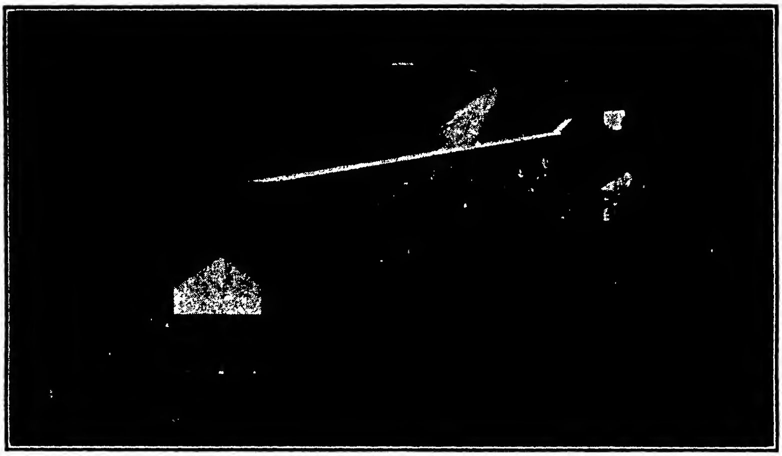

Fig. 16.—Mine and plant of American Phosphate Corpn., Montpelier, Ida.

and all Pacific ports by establishing a special terminal fully equipped with storage bunkers, bins, loading machinery, etc. The Union Pacific System transports the phosphate from the Idaho field to this terminal. The storage facilities consist of eight concrete bins that have a combined normal capacity of 18,000 tons of phosphate rock, with delivery to vessel at the rate of 300 tons per hour, through two traveling ship's towers operating along the harbor face of the pier. In addition to an extensive belt conveyor system, a special box-car unloader is provided; this discharges the contents of a box car into a hopper in less than 8 min.; two Merrick weightometers have been installed and check the materials handled with an accuracy of 99 per cent. Long wagon hauls and a general inaccessibility of much of the Idaho deposit is another factor that retards marketing.

Tonnage in Reserve

The original western phosphate reserve was set up on Dec. 9, 1908, but has been added to and reduced a number of times. Idaho had in

January, 1924, 720,534 acres of phosphate land in this reserve. In the tonnage estimates offered by the United States Geological Survey, only the main bed is considered and some high-grade and all low-grade rock was excluded. Many areas have not been examined thoroughly and may add much to the total; figures for Idaho up to 1923, as given by the United States Geological Survey, are 4,997,717,000 tons in reserve. From inspection of the field, the writer believes that a tonnage estimate of 5,500,000,000 is not too great.

Development and Production

The development of the Idaho deposit has resulted in the entry into the field of six responsible companies. The San Francisco Chemical Co. began operating in 1907 under the supervision of Jos. J. Taylor who has done much toward stimulating development. Although all the companies have large holdings and have spent large sums of money, the Anaconda Copper Mining Co. has been the most progressive. It has established the townsite of Conda and built approximately 50 houses and cabins for its employees, as well as offices, bunk houses, a boarding house, a recreation hall, and a schoolhouse. A water system, refrigerating system, and railroad connections with Soda Springs 8 miles to the west, make this one of the most modern mining camps in the state.

The production is as yet not large and has been estimated to be 205,000 long tons, up to Jan. 1, 1924. However, this potential industry of southeastern Idaho, when running at full blast, will dwarf the now famous Coeur d' Alene or Butte districts, as it will prove to be one of the most important factors in American industrial progress. With these deposits the existence in the future of American agriculture is guaranteed, provided potash and nitrogen are available.

Idaho Phosphate Companies

The American Phosphate Corpn., which is capitalized for $100,000, has its offices at Salt Lake City. The mine is located about 4½ miles east of Montpelier, in Bear Lake County. The underground development consists of about 2000 ft. of drifts and tunnels. The property consists of a lease of five claims secured from the San Francisco Chemical Co. The plant is gas driven and contains complete crushing and drying equipment with two 25-hp. F.M. engines, one No. 4 Gates gyratory crusher; one 45-ft. American dryer, and one 95-ft. 18-in. conveyor. The plant employs from four to six men and has produced each year since 1920. The wagon haul is 4½ miles to the railroad.

The Anaconda Copper Mining Co. has the largest plant in the area. The mine is located at Conda, 8 miles east of Soda Springs in

Caribou County. The underground development includes 1335 ft. of drifts, 3050 ft. of crosscuts and tunnels, and more than 500 ft. of raises; 1400 ft. of heavy timber trestles connect the mine with the storage bins. The mine tracks are 36-in. gage and 60-lb. rails. Two 16-ton storage-battery locomotives pull the long string of 10-ton side-dump ore cars. Armstrong Shuveloders load the ore at the face. The property consists of a block of 23 claims, comprising 3403 acres, 8 miles of railroad connecting Conda with Soda Springs, a complete crushing and drying plant with a capacity of 450 tons per day, a power plant 50 by 50 ft., with steel and granite construction, an Ingersoll Rand 1000-cu. ft. compressor; motor-generator set; one 450-kv. a. 44,000/2300-volt substation with three auxiliaries, one 3000-ton gunite storage bin with conveyor; one 420-ton crude-rock feeding bin, one 1000-ton dried-rock storage bin, one No. 12 Traylor bulldog gyratory crusher, several 22 by 54-in. Anaconda crushing rolls; one class A-12 Ruggles Cole dryer, one Vezin sampler and miscellaneous conveyors, elevators, and shaking feeders. All equipment is motor driven. A refrigerating plant is also operated. This company has produced since 1920 and has often employed as many as 115 men.

The Bear Lake Phosphate Co. is situated at Paris; the mine lies 1½ miles west of Paris in Bear Lake County, Idaho. The underground development consists of 1500 ft. of electric-lighted double-track tunnel and an additional 1200 ft. of crosscuts and drifts. The property consists of 317 acres of patented land and 360 acres leased from the government. The plant includes a 1000-ton storage bin, one 160-cu. ft. electrically driven air compressor, and complete equipment for mining. The installation of a large mill is being considered. Operations began late in 1919 and lasted until 1923. About 10 men are employed when operating. The wagon haul is 1½ miles to the railway at Paris.

The Idaho Phosphate Co., which is the successor to the Western Phosphate Co., has offices at Salt Lake City, Utah, and at Paris, Ida. The mine is 3 miles southwest of Paris in Bear Lake County. The underground development is extensive and includes 3000 ft. of tunnels, drifts, crosscuts, and winzes, besides 40 stopes each 250 ft. long. The property includes patented claims to the extent of 240 acres. A modern and complete mine plant includes compressors, machine shop, a large and fully equipped drying and crushing plant, electric power is provided for all equipment, and the company owns 3¾ miles of railway extending from the mine to Paris. The mine has been idle since 1920.

The San Francisco Chemical Co. owns the Waterloo mine with offices at San Francisco, Calif., and at Montpelier, Ida. The organization is capitalized for $200,000. The Waterloo mine is located 3 miles east of Montpelier in Bear Lake County. The underground development amounts to about 3000 ft. of tunnels and drifts approached by three adits. The property consists of ten patented claims comprising 505

acres. There are three storage bins, a blacksmith shop, and a ventilation and compressor plant. This mine was a steady producer from 1907 to 1920, but has been idle since 1921.

The Utah Fertilizer & Chemical Manufacturing Co. is capitalized for $100,000. The mine and property lies 8 miles east of Georgetown, Ida., in Bear Lake County. The underground development is limited to tunnels and two shafts, amounting to 525 ft. The company owns sixteen patented claims, totaling 2316 acres, and includes some of the richest phosphate rock in the state. Development has been hindered by an 8-mile wagon haul to the railroad.

Acknowledgments

The writer acknowledges his indebtedness to Mr. Alfred L. Anderson for assistance in preparing and compiling most of the tables; also to Mr. Jos. J. Taylor, of Montpelier, Ida., and Mr. C. E. Nighman of Conda, Idaho, for photographs, information, and courtesies extended during field work. The writer also pays tribute to the monumental, but largely unpublished, work in this area of Mr. George Rogers Mansfield, of the United States Geological Survey.

DISCUSSION

F. A. Wilder, North Holston, Va.—Reference has been made to the manufacture of superphosphates by the volatilization method. Many of us who were at the Birmingham meeting last fall were impressed by two papers on that subject. The possibilites of making superphosphate by this method are promising and it may reasonably be expected that something of substantial importance will be developed by this means, which will make more available the more remote phosphate deposits.

S. L. Willis, Corning, N. Y.—Some time ago, we made for one of the Middle West cement companies Pyrex glass insulators to replace porcelain in the Cottrell dust precipitator, the assumption being that porcelain was not giving satisfaction. The glass insulators were brick shaped 13½ by 9 by 2⅜ in. I believe that they are used in stacks of six or eight to obtain the desired height. The insulation ordinarily used in Cottrell systems is a pillar type varying from 24 to 36 in. in height.

At the present time both types of insulator are manufactured in Pyrex glass, and there is an opportunity for considerable saving if the latter can be substituted for the former.

As the troubles experienced have been due to the corrosive action of the potash in the cement dust, there would seem to be no reason why the pillar type of insulator should not give satisfactory service. If, on the other hand, the contour of the pillar type insulator has proved to be unsat-

isfactory in this service, the increased discharge path of the brick type insulator is sufficient reason for its use.

G. R. Mansfield, Washington, D. C. (written discussion).—The writer is not sure of the author's meaning, in the first paragraph, where he states that "The African deposits, although benefited by a water haul, have the disadvantage of being isolated from a source of acid so that the crude rock is shipped from Africa to its destination, whereas in the United States the chief product shipped is acidulated rock or various types of superphosphatic fertilizers." There would seem to be little point in comparing external shipments from Africa with internal shipments in the United States. He is probably comparing shipments of African phosphates with shipments of American phosphates to foreign markets. If so, figures available at the U. S. Geological Survey Office show that in 1923 (figures for 1924 are not available) superphosphates (acid phosphates) exported from the United States amounted to 42,156 long tons and that shipments of fertilizers of all sorts, including superphosphates, were only 269,061 long tons; whereas exports of phosphate rock in the same year amounted to 827,551 long tons. The phosphate produced in the United States in 1923 was 3,054,149 metric tons compared with 467,-384 for Algeria; 25,370 for Egypt; 225,395 for Morocco; and 2,338,000 for Tunis; or a total of 3,056,149 for northern Africa. The western phosphate field, including Montana, Wyoming, and Utah as well as Idaho, has frequently been referred to as probably the largest phosphate field in the world. Whether, as stated on page 316, Idaho without the aid of its sister states may claim this honor is perhaps more questionable.

On pp. 317–321, the geology of the region is briefly summarized and the character of the phosphate is briefly described and a chemical analysis is cited. No mention is made of Mississippian phosphate, except a brief tabular reference, although at one locality at least beds of high quality assigned to this period are apparently present in commercial quantity.

On pp. 321–323, the origin of the phosphate is discussed and the writer's opinions published some years ago are cited. Since the publication of that article the writer has had opportunities for further study and has found it necessary to change some of his conclusions. From present data, there seems little doubt that the phosphatic oolites were formed directly from phosphatic solutions or colloids on the sea bottom and were accumulated into sedimentary rocks, just as sand grains or other clastic materials are built into sedimentary formations. Space is insufficient to discuss adequately the conditions leading to the formation of the oolitic phosphate beds. The writer has embodied his views in a detailed report on the phosphate field of southeastern Idaho, now awaiting publication as a Professional Paper of the Geological Survey.

On pp. 326–327, where processes for volatilizing phosphoric acid are discussed, it would have been appropriate to mention the commercially successful electric furnace methods now in operation by the Federal Phosphorus Co. at Anniston, Ala.

On p. 332, it should perhaps be added that the construction of the shipping facilities at Portland was begun in 1920, when phosphate mining throughout the phosphate districts of the country was booming. Orders from Japan gave rise to the hope of considerable oriental business. This business has largely declined and in the face of cheaper, water-borne, high-grade phosphate from the Pacific islands, it may not soon be revived.

On pp. 332–333, tonnage estimates are briefly mentioned and the U. S. Geological Survey's estimates are raised approximately 10 per cent. The Survey's figures are admittedly conservative. They represent totals actually used in classifying the public lands under standard procedure, which recognizes thickness, quality, and depth of beds in the light of geologic structure.

On p. 335, general acknowledgments are made. A little more specific acknowledgment through the text would be desirable. For example, three of the U. S. Geological Survey's photographs are used as illustrations but they are not distinguished from those supplied by mining companies or those taken by the author.

R. W. Stone,* Harrisburg, Pa. (written discussion).—At the end of the first paragraph, the author says: "The African deposits, although benefited by a water haul, have the disadvantage of being isolated from a source of acid, so that the crude rock is shipped from Africa to its destination, whereas in the United States the chief product is acidulated rock or various types of superphosphatic fertilizers." One surmises that, in this sentence, the economics of the deposits in North Africa and the United States are being contrasted. If this is meant, one might suppose that the phosphate-rock industry in the United States does not have the advantage of water transportation. About 85 per cent. of the phosphate produced in the United States comes from Florida, and about 80 per cent. of Florida's output is shipped by boat from Jacksonville, Port Tampa, Tampa, and Boca Grande. In other words, with a production of 2,500,000 tons, only 500,000 tons leaves Florida by rail. Florida furnishes such a large proportion of the production of the United States that the phosphate-mining districts in Tennessee and Idaho need not be considered; therefore, the African deposits do not have any particular benefit by a water haul if it is intended as a contrast with the phosphate rock industry in the United States. A fleet of steamers for years has regularly carried phosphate rock from Florida to Norfolk, Va.; Baltimore, Md.; Carteret, N. J.; and other points on the Atlantic Coast.

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* Assistant State Geologist.

Do the African deposits have a disadvantage by being isolated from a source of acid? Most of the plants in the United States making fertilizers from phosphate rock are in states bordering the Atlantic and most of those that make their own acid derive it from pyrite mined in Spain or from sulfur produced in Louisiana and Texas. The North African phosphate is sold mostly in southern Europe, where Spanish pyrites and Sicilian sulfur are comparatively close at hand. In other words, the source of acid for many of the fertilizer plants in the United States is much more distant from the place where utilized than are the African deposits from the sources of pyrite and sulfur, and the disadvantage of the African deposits seems questionable.

Lastly, the statement seems to be that Africa ships crude rock and that in the United States the chief product shipped is acidulated rock or superphosphatic fertilizers. To be comparable, the statements should refer to the same thing. If it means shipments from the two countries, the tonnage of raw rock exported from the United States is several times that of the acidulated rock or superphosphate. If the contrast is in character of the rock shipped from mining localities, the rock leaving the phosphate mines in the United States is just as raw as that leaving the African mines. This last comparison, therefore, seems to be without good foundation and the whole statement is subject to revision.

L. K. Armstrong, Spokane, Wash.—The discussion is really confined to two criticisms: The first respecting the relative marketing advantages of African and Idaho deposits; the other a disclaimer of the present importance of Idaho deposits and competition with those near the South Atlantic seaboard. The principal factor, however, and one of greatest ultimate importance, is the significant relative tonnages of those in southern Idaho (and I might add those in northeastern Utah and southwestern Wyoming) as compared with those in the southeastern United States, and in other countries. I was deeply impressed with the statement that more than 5,000,000,000 tons exists as reserves in southeastern Idaho, this figure being somewhat reduced in U. S. Geological Survey estimates. I have no doubt that these estimates will be found as nearly correct as the more conservative estimate of the Survey.

Manufacturing Problems of Cement Industry

By John J. Porter,* Hagerstown, Md.

(New York Meeting, February, 1925)

The requirements of the standard specifications under which Portland cement is sold have materially increased within the past 10 years, but practically all companies are now furnishing cement better than these requirements; in some cases exceeding them by nearly 100 per cent. From a sales standpoint, it is desirable to have a product that is uniform to a high degree and free from occasional quality troubles. A failure in quality, even if it affects only a few hundred barrels out of a yearly output of a million or more, is apt to be talked about in the trade and to affect the salability of the entire output. For these reasons, there has recently been great activity along the lines of quality control and improvement; and some of the most interesting problems of the industry are in this field.

From the manufacturing standpoint, the quality of cement is chiefly a matter of uniform and proper chemical composition of the raw mix fed to the kilns plus proper burning in the kilns; the fineness to which the cement is ground, the proportions of gypsum, the method of seasoning, and the like are contributory factors.

Uniform chemical composition of the raw mix has been one of the most difficult problems to solve. Most plants will use from 1000 to 3000 tons of rock per day and in but few cases is this material as it lies in the quarry even approximately uniform in composition. The problem, then, is to quarry and mix this raw material in such a manner that every handful passing through the kilns will have practically the same analysis as every other handful. To accomplish this purpose there are two methods of preparation: the wet and the dry.

In each process, a stone storage is the first requisite of a successful plant. This storage place may handle the stone before or after crushing; its capacity may vary from two to three days' up to several months' supply, but it should be so designed that it can be filled as desired by the chemist and drawn at such points as will give a mixture of the various kinds of stone coming from the quarry and a reasonably uniform material going to the mill. The size of the storage place and the method of handling should be varied according to the nature of the material.

* First Vice-president and General Manager, Security Cement & Lime Co.

Following the stone storage, the two methods of manufacture diverge. In the wet process, the raw material is ground with enough water to make a thick slurry, which is stored in tanks and stirred so that the contents of any one tank will be absolutely uniform. The chemist, after analyzing each tank, can then mix the slurry so as to obtain a raw material for the kilns of practically uniform composition. In the dry process, the storage tanks are arranged so as to be filled in rotation and drawn together, thus ironing out the variation occurring from hour to hour in the stream of material; the final stage in this mixing process is usually storing, in what are known as silo tanks, the ground raw material before it is fed to the kilns. As each tank is filled, it is sampled and analyzed; two or more of these tanks are then drawn together in proportions to give exactly the composition required in the kiln feed.

After many years of experience with these processes there is a wide difference of opinion among cement-mill operators as to their relative merits. It is generally conceded that uniformity of mix is obtained somewhat easier with the wet process and there is some advantage in the cost of grinding the material wet. On the other hand, there is a decided economy of kiln fuel in the dry process and, in the writer's opinion, the full possibilities of obtaining uniform material through use of a series of mixing bins in the dry process are not generally appreciated or realized.

Effect of Variation in Chemical Composition

The raw material fed to the kilns must be uniform in composition and of the right composition. This might seem to be a simple matter, but small differences in the proportions of the lime, silica, alumina, iron, and magnesia are inevitable; further, what is the right composition at one mill is not necessarily the right composition at another. In other words, the proper chemical composition for high-quality cement apparently depends, to some extent, on the nature of the raw materials being used. The reason for this fact, if it is a fact, and the exact relations involved are not well understood, but it is probably these factors, which can only be worked out by experience, that are largely responsible for the quality difficulties of so many plants during the first year or two of their operation.

The effect of some of the occasional, but less common, constituents of limestone on the quality of cement is not thoroughly understood. It is believed that the presence of appreciable amounts of phosphoric acid may, at least under some conditions, affect the quality of the cement. Whether this trouble is inherent in this element or whether it is due to the acid combining with a certain proportion of the lime and thereby making a necessary change in the proportions of the mixture is not known. It is thought that considerable quantities of potash and soda in the raw material may also affect the quality of cement, although this has not been proved and there are only indications to that effect.

Importance of Correct Burning

The degree of burning is a quality factor of the greatest importance and is the one thing, perhaps, most frequently causing trouble. As fuel is one of the major items in the cost sheet, there is naturally a tendency to economize as much as possible in its use; occasionally this leads to a degree of underburning that affects the quality of the cement made. This is particularly the case as there is no satisfactory method of measuring or recording and, hence, of standardizing the degree of burning. The methods generally used to check up burning are visual inspection of the clinker as it issues from the kilns and a test similar to the soundness test on cement made on the ground fresh clinker. Attempts have been made to use radiation pyrometers to measure the temperature of burning, and in that way control it. But, the burning of clinker is a function of time as well as temperature; in fact, it is by the time of exposure that the degree of burning is ordinarily controlled, the temperature being nearly constant and fixed by the nature of the fuel and the conditions of its combustion. There is a wide range between the minimum degree of burning, which will just get the cement past the specifications, and the maximum degree, which will produce the best cement that can be made from a given material. Any burning in excess of the latter is overburning; overburned clinker will grind into perfectly good cement, the only objection to it is from the standpoint of cost. There is a danger in underburning, however, and one of the most interesting and important problems of the industry is to establish means of control that will enable the operator to know for a certainty when he is burning at the most economical point.

Research Work Now Being Done

An interesting problem is the possibility of producing a super-cement one having a materially greater strength than is now the practice, by carrying the lime in the mixture a little higher than at present, burning correspondingly harder, and grinding much finer. Much work has been done along this line, especially in Germany, but there is much more work to be done. Within the past year, a research organization, supported jointly by the Portland Cement Association and the Bureau of Standards, has been established to study the fundamental chemical problems of cement. It is hoped that the result will be a better understanding of many things that are now puzzling the practical operating men of the industry.

Factors Affecting Cost

The principal factors in the cost of making cement are in the approximate order of their importance, labor, fuel, power and repairs; the principal operations into which these factors enter are quarrying, crushing,

grinding and burning. Rapid progress along the line of cost reduction has been made during the past decade. Ten years ago, somewhat over one man-hour of labor was required to make a barrel of cement; at present the average is only a little over one-half man-hour, as a result of the use of larger units, improved machinery, and the standardization of methods. The introduction of waste-heat boilers has also resulted in a material saving in cost at many plants. With this equipment, power can be generated at a cost of from 0.6–0.8 cents per kw.-hr., a considerable reduction from the usual cost when using coal-fired boilers. In other words, the use of this equipment has reduced the total fuel consumption approximately 50 lb. per barrel.

The effect of this technical progress is to be seen in the relatively lower price of cement, compared with other structural materials. There was, of course, a great increase in the price of all building materials during the war and in the subsequent period but statistics compiled by Government Bureaus show that from 1912 to 1921 the price of Portland cement increased less than that of any of a large number of materials used in building and construction, and very much less than the average of all of them.

The most interesting and valuable work on the grinding problems of the cement industry has been done by the research engineers of the Conservation Committee of the Portland Cement Association. This work, so far, has been confined to the grinding of clinker in tube-mills but it has shown the fallacy of many generally accepted ideas. For example, it has been shown that the ratio of lime to silica, iron, and alumina is the one chemical factor affecting grindability, and that the silica, iron and alumina ratio, which for so long was considered important, is really of no effect. Another exposed fallacy is the effect of seasoning on grindability. The temperature of the clinker is of great importance but starting with cold clinker, exposure to the elements, resulting in increase in "loss on ignition," is detrimental to grindability.

A number of important problems relating to grinding remain to be solved. The exact operation of temperature, in its effect on grinding of clinker, is not understood. We do not know if the data relating to grindability in tube-mills can be applied bodily to other types of mills or whether it will be necessary to modify these data for each kind of grinding mill. Neither do we have adequate and systematic data regarding the relative efficiency of the various types of grinding mills on the various materials that must be ground. Experience in the industry would seem to indicate that certain mills may work efficiently on one material and may be very unsatisfactory at another location and on other materials.

The burning of the cement clinker is the heart of the manufacturing process and some of its most interesting and important problems are found here. Since the adoption of the rotary kiln, tremendous progress

has been made in burning efficiency; but our knowledge of the process is still largely rule-of-thumb and there is great need for a systematic study of kiln operation and the reduction of its various factors to a quantitative basis.

There is no really satisfactory expression for kiln output in relation to kiln size. Attempts have been made to rate output on the basis of kiln volume, shell area, area of cross-section at the burning zone, etc.; none of these methods will hold for all sizes of kilns. It is self-evident that for a given material the output will, within certain limits, be proportional to the amount of coal that can be burned per unit of time; or, in other words, to the area of cross-section in the burning zone. It is also evident that the longer the kiln, the better prepared will be the material when it reaches the burning zone; hence, less fuel will be required per unit of output and the output will be larger for a given rate of combustion of fuel. It is also evident that the feed end of the kiln must have an area sufficient to pass the gases of combustion at the available draft. It should be possible to work out the relationship of these various factors and to devise a formula that, for a given material and a given draft, will accurately express kiln output in relation to dimensions.

A somewhat related problem is the relationship between output and fuel economy. For very low outputs radiation loss, being constant per unit of time, is excessive per unit of output; hence, fuel consumption is increased. For very large outputs, involving a high rate of combustion of fuel, the time of contact and the opportunity for heat transfer between hot gases and incoming material are lessened, hence, fuel consumption is increased. Between these extremes lies the most economical rate of production from the standpoint of fuel economy. This rate no doubt varies somewhat for different materials, but quantitative data, which are almost totally lacking at the present time, would be of great value to the industry.

One of the most interesting problems is the effect of small variations in chemical composition and nature of raw materials on the output and fuel economy of the rotary kiln. It might be supposed that with a constant chemical composition all materials would burn the same, but this does not seem to be the case. Apparently, the form in which the silica, and perhaps other elements, is present in the raw material has a most important bearing on the ease of combination; as a result, at different plants the same size kiln produces widely varying outputs with widely varying fuel economy. Even at the same plant, in many cases, the output and fuel consumption vary from week to week and from month to month, according to the strata being taken from the quarry. There is great need for a simple test for "burnability" of raw materials so that these differences can be measured and predictions made in advance of the

utility of new materials. Such a test would also be of great use in existing plants in adjusting a three-component mix to the most efficient point.

It is self-evident, and has been known for many years, that the fineness of grinding of the raw material affects the ease of burning but there are not sufficient quantitative data to enable the manufacturer to calculate closely the most economical point of grinding, everything being considered. The problem of the effect of fineness of coal is being solved by the engineers of the Conservation Committee of the Portland Cement Association. It has long been supposed that the finer the coal the greater is the fuel economy, but the committee has found that in many cases there is no advantage in grinding finer than approximately 50 per cent. through the 200-mesh sieve. Under usual operating conditions, this fineness is sufficient to burn perfectly all the coal; and when all heat units have been released obviously there is nothing further to be gained. An incidental advantage of the use of coarser coal is the greater ease of handling. In some plants, the indirect saving through relative freedom from coal floods and spontaneous combustion in coal bins is an important factor. On the other hand, the use of coarse coal has not been satisfactory at some plants where it has been tried. There are, evidently, certain conditions necessary for its success that have not been determined, but the problem will no doubt be completely solved in the near future.

There is, apparently, no such well-defined critical temperature in the operation of cement burning as exists in the iron blast furnace. Nevertheless, a high temperature is necessary and sufficient heat units must be furnished at this high temperature to make up for the radiation losses and heat carried out in the clinker. A number of experiments looking toward higher temperatures of combustion, principally through the use of preheated air, have been tried; while the results are conflicting, there seems to be some advantage in this practice. A mathematical study, similar to that made by Johnson[1] for the iron blast furnace would be a valuable guide to work in this field.

Along the same line is the problem of the insulation of the burning zone of the rotary kiln. This has been repeatedly tried; the failure of the experiments was due to the difficulty of holding the lining. Ordinary firebrick lining owes its stability to the cooling of its outer surface by radiation from the kiln shell, and when this is prevented, its life is only a matter of a few hours. No manufacturer, so far as known, has tried a lining of radically different composition and more refractory character in combination with an insulating material in the burning zone.

The industry still has much to learn concerning kiln linings. It is customary, in rotary-kiln operation, to form a coating of fused clinker on the surface of the firebrick lining, which coating forms the real working surface. The life of the lining is, in most cases, dependent on its ability

[1] *Trans.* (1906) **36**, 454.

to hold a coating and, generally speaking, refractories high in alumina are the most satisfactory. There is a wide difference in cost between the various brands of high alumina kiln blocks and, as the action of the coating differs with the various materials being burned, each plant must work out the problem of the most economical lining for itself. With our present knowledge this is a long and expensive procedure because we have no correlation of the results of laboratory tests with the results of actual experience.

A most important problem in connection with kiln operation is that of getting a perfectly uniform feed of both raw mix and powdered coal. When feeding dry raw mix, the amount passed per revolution of the feed screw varies within wide limits according to the condition of the material. Mix that has been freshly ground is still warm, contains a large amount of entrained air, and will weigh much less per cubic foot than mix that has been allowed to stand for some time in storage tanks and is therefore cold and relatively free from air. Morover, mix feeds more freely into the feed screws while the tank above the screw is being filled; also the rate of feed varies with the height of material in the tank above the screw. Various devices are in use to prevent flooding of raw material entering the kilns but none give that perfect uniformity in rate of feed which is essential to the best output and fuel economy.

A similar condition prevails in respect to the feeding of the pulverized coal, and there is the additional disadvantage that any variation in the rate of feed makes it impossible to adjust the air supply to the most efficient point for perfect combustion. In addition to the fluctuations occurring from hour to hour, there is a fluctuation from second to second due to the action of the feed screw, some coal being pushed into the blast pipe each time a conveyor flight moves across the feedpipe outlet. Double- and treble-flight conveyors are used to lessen these intervals but even then, in many cases, there is an appreciable puffing of coal at the nozzle of the burner pipe resulting in a quick succession of too much and too little air for perfect combustion.

Dust Collection and Prevention

Among the most important mechanical problems of the cement industry is dust collection or prevention. This is important from the standpoint of working conditions at the plant itself and, in many instances, from the standpoint of community nuisance. There are many sources of dust in the cement mill but the more important, in the order of their importance, are the kiln stacks, dryer stacks, grinding mills, crushers, and conveyors. There is no gainsaying the fact that the wet process has a material advantage from this standpoint. Dryer dust is eliminated, with the exception of the coal dryers, and dust from raw

grinding is entirely eliminated. From the kiln stacks, the dust loss in the wet process should be, and usually is, materially less than in the case of the dry process, although this is not always the case.

Several types of bag filters and centrifugal dust collectors are available in connection with grinding mills, crushers, and conveying machines. Generally speaking, they work with a fair degree of efficiency, except where the dust is associated with a certain amount of steam. For kiln stacks, Cottrell electrical precipitators are satisfactory, although relatively expensive in both first and operating cost. In a number of cases, centrifugal collectors have been installed following waste-heat boilers. They usually catch only 60 to 80 per cent. of the dust, but are relatively inexpensive in installation and operation and, hence, are most satisfactory where they will answer the purpose. There is no satisfactory dust collector for use on dryer stacks, the combination of steam and dust being particularly hard to handle. A few attempts have been made to scrub these waste gases with water spray, but this procedure is only feasible where an abundant supply of water is available.

Among the multitude of other problems are those having to do with the life of grinding mill and conveyor parts. The rapid growth of the cement industry has only been possible through the development of grinding machines permitting the pulverizing of the enormous quantities of materials required. These materials are highly abrasive, replacements of mill and conveyor parts form a large item in the cost and the problem of better materials is important. This problem is primarily one for the manufacturers of mill machinery but, in view of the enormous variation in the life of different lots of roll heads, grinding rings, etc., the cement industry may be forced to delve into these matters and work out its own metallurgical specifications.

Rotary Calciners for Gypsum

FRANK A. WILDER,* NORTH HOLSTON, VA.

(New York Meeting, February, 1925)

THE most important process in a gypsum mill is calcining the crude mineral. There seems, however, to be little progress or change in calcining methods. This would not be surprising if the industry was not, in other ways, developing. The demand for gypsum in its various forms, however, is growing rapidly. The output has more than doubled in six years, while the value of gypsum products, through the introduction of higher priced specialties like wall board, has nearly trebled in the same period.

In other industries, under somewhat similar conditions, calcining in rotating cylinders, either by direct or indirect heat, has replaced the method that still prevails in gypsum mills. Efforts were made to use rotary calciners in manufacturing plaster of Paris in the early days of the industry in America; 25 years ago rotary calciners were in use in Germany. At that time there was great diversity of opinion in regard to their merit.

In 1923, the output of calcined gypsum in the United States was 3,101,378 tons. About nine-tenths of this material was calcined in kettles, the remainder in rotary calciners. The ratio was about the same 10 years ago. During these 10 years, rotary calcining made relatively no gains, and there were no important changes in the construction of kettles. In their manipulation, the only change of consequence was in connection with the length of time that the gypsum is left in the kettle. For wall-plaster purposes, all producers who had not previously done so changed from second-settled to first-settled calcined gypsum, thereby reducing production costs and improving the plasticity and sand-carrying capacity of their plaster.

Nevertheless, in the few mills in which they were installed, rotary calciners continue to operate, with possibly one or two exceptions, and to be highly successful. In these 10 years, the Cummer type of rotary calciner has disappeared. All rotaries now used are of the cement-mill type with a diameter of 6 or 7 ft. and length of 80 to 120 feet.

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Producers with mills in two or more localities, who are operating rotary calciners in one district yet persist in using kettles in other districts, are in the best position to discuss the relative merits of these methods. They have cost data and ample experience in regard to the quality of the finished product. Their discussion and criticism of this paper will be most welcome.

In order that the facts may be more fully brought to light, it seems desirable to present such information as is available as a basis for discussion. As a preface to such a discussion the uses of calcined gypsum, and the peculiar properties desired in connection with these uses, may profitably be considered. In the order of their importance these uses are:

Wall plasters: Hair fibered (often called cement plaster); wood fibered.

Structural gypsum: For gypsum wall, roof and floor tile; for poured-in-place roofs and floors.

For wall and plaster board.

For Portland cement.

Specialties: Finishing plasters; casting plasters; molding plasters; dental plasters, etc.

For retarding Portland cement, raw gypsum is commonly used. A few cement mills, however, prefer to use calcined gypsum. In this material a uniform chemical analysis is all that is desired.

In general, the properties desired in calcined gypsum are tensile and compressive strength, hardness, plasticity, and definite and uniform setting time. Certain of these properties are much more essential for calcined gypsum in some of its applications than for others. Plasticity, for instance, which is highly essential in hair-fibered wall plaster intended for use with considerable quantities of sand, is not so important when the material is used in making tile or wall board. On the other hand, compressive strength, which is of importance in connection with structural gypsum is not so essential in gypsum wall plaster.

The demand for plasticity in wall plasters varies with the character and quantity of sand that is used with it. If the calcined gypsum lacks plasticity with a given amount and kind of sand, the mortar works "short." With less sand or sand containing more loam, it may work exactly right. If there is an excess of plasticity in the mortar after mixing, it is sticky and gummy, adheres to the workman's tools, and is quite as objectionable as though it worked "short." Highly plastic calcined gypsum is not acceptable in wood-fibered plasters that are intended for use with little or no sand.

The average calcining kettle consists of a metal cylinder 10 or 12 ft. in diameter and 10 ft. high, with arched cast-iron or steel bottom. Four flues traverse the cylinder horizontally. The sides are jacketed and bricked in such a way that the heat from the firebox located under the kettle is drawn up through ports into the space between the kettle shell

and the outer brick jacket, thence through the flues into the stack. Considerable draft, always natural, is used in order to take most of the heat away from the bottom of the kettle and distribute it to the sides and to the flues. Mechanical agitation aids in bringing fresh gypsum in contact with the heated surfaces. Even more important as a means of agitation is the boiling of the gypsum as it gives off steam in parting with its water of crystallization.

In gypsum calcined in kettles two distinct products are recognized, depending on the temperature used in the process. The structure of the calcining kettle permits of sufficient temperature control to produce either product at the option of the operator. First-settled calcined gypsum is drawn when the temperature reaches 325° to 340° F. while second-settled is discharged from the kettle at 390° F. The first-settled material consists largely of the hemihydrate $2CaSO_4.H_2O$, while second-settled is for the most part soluble anhydrite, $CaSO_4$. This soluble anhydrite is wholly different from dead-burned gypsum formed by long calcining at temperatures in excess of 400° F. It is quick setting, has higher tensile and compressive strength, and is less plastic than gypsum drawn at 325°–340° F. It changes to the hemi-hydrate on exposure to the air.

Recording thermometers are in common use in connection with gypsum calcining kettles, but even without this guide the expert calciner can tell by the behavior of the gypsum in the kettle when the degree of calcination that he desires has been attained.

For those uses where high tensile and compressive strength are essential and where plasticity is not especially sought, second-settled calcined gypsum is in demand. For almost all purposes, however, the strength of first-settled stucco is ample and, on account of its lower cost, it is used wherever possible.

About 20 years ago the Cummer process, in which a rotary calciner was a feature, was introduced for treating gypsum, and was used in New York state for about 15 years. One small plant of this type is still operating in Mexico City. In the Cummer process, heat was applied to the gypsum as it passed through a rotating cylinder. The movement of the smaller particles was hastened through the cylinder by a fan. The gypsum, hot from the calciner, was allowed to stand for several hours in air-tight bins. The purpose of this was to permit a readjustment of the chemically combined water. Some of the gypsum was undercalcined and the cores of the larger lumps were not calcined at all; some was overcalcined and lost all of its water. It was believed, and the results obtained indicated that there was some measure of truth in the proposition, that the undercalcined portion of the mass in the bin would in time contribute a portion of its water of crystallization to the overcalcined and, if drawn from the bin at the proper time, the entire mass would be in the desired hemihydrate form.

The calcined gypsum produced by the Cummer process was often erratic in set, and required unusual amounts of retarder, indicating the presence of some raw gypsum. However, the product was very plastic. It had unusual bulk after grinding and was acceptable to the plaster trade in spite of its occasional bad behavior in the way of erratic set.

The producers who used the Cummer process gradually discovered that they could secure the same, and even better, results with less cost in rotary kilns of cement-mill type, and without the expense and delay of storing in sweat bins. Raymond mills grind the hot gypsum as it comes from the calciner. In this fine state, molecular readjustment evidently takes place in the mill, in the storage bins and along the screw lines. Certain mills in New York state are producing calcined gypsum for wall-plaster manufacture by this process at the present time.

When the Emley process for making gypsum more plastic was introduced 3 years ago, it seemed particularly adapted for use with a rotary calciner. As described in the patent that was issued to W. E. Emley of the Bureau of Standards, the process is one "of increasing the plasticity of calcined gypsum which consists of grinding the calcined gypsum to eliminate the water content during the grinding operation, preventing the escape of the said water content during the grinding step and continuously keeping the above treated gypsum in contact with the water thus eliminated, ceasing the grinding operation and permitting the water thus eliminated to be reabsorbed."

One of the more recently constructed mills in New York combined a rotary calciner with a ball-mill operating in closed circuit for grinding. The results were somewhat in line with expectations, but developed some troublesome and wholly unexpected features. An exceedingly plastic calcined gypsum was produced. One characteristic of such plastic material is that it packs like damp snow. It refused to flow through spouts or to move satisfactorily in the ordinary conveyors. When mixed with the customary quantities of sand, it made a mortar that was too sticky. It could not be worked in the form of neat wood-fiber plaster. The ball-mill was opened to permit a free circulation of air and the situation was somewhat relieved.

The interesting question now is whether rotary calcining can be successfully introduced in other gypsum fields. The outstanding fact is that this method of calcining, with perhaps one exception, is confined to the western New York field. It is possible that the physical characteristics of the gypsum of western New York have some bearing on the question. This gypsum seems to make fewer fines in crushing than the gypsum of some other localities. On account of the low temperature and the ease with which gypsum calcines and the difference in the nature of the product produced by relatively small change of temperature, to secure uniformity the material fed to the rotary calciner should vary in

size as little as possible. Results comparable to those secured in New York might be secured elsewhere if the gypsum were crushed to pass a 1-in. ring and everything passing a 1/4-in. ring calcined separately and at a temperature lower than that used for the larger lumps.

The saving in operation costs is estimated by different individuals in the gypsum plaster business, all the way from twenty-five cents to one dollar. If it were necessary to double the installation in order to treat the fines separately, the additional operating and maintenance cost with interest and depreciation must be taken into account as an offset to saving in operation.

For a plant of ordinary capacity that must manufacture some second-settle stucco, finishing plaster, or any of the gypsum products for which gypsum calcined in a rotary is not adapted, the installation of a rotary calciner does not seem practical as the expense of installing and operating two systems would be burdensome. In a plant where the equipment may be considered from the standpoint of wall-plaster production alone, the installation of rotary calciners may be regarded as an open question. The plasticity desired can be obtained by other means, and in ways that will permit of variation to meet the sands of different markets. Unless there is ample capital and demand for output sufficient to justify the installation of a separate installation to handle the fines, the use of a rotary calciner in a field where the gypsum crumbles easily is not wise in the light of existing information.

DISCUSSION

L. K. Armstrong, Spokane, Wash.—I was impressed with what the speaker said in connection with the sizing; two other factors were not mentioned; these were time and temperature. Applying one against the other, it would appear to me the better solution of the problem of successful rotary installation would be proper sizing, time, and temperature.

Limestone Production as a Mining Problem

By J. R. Thoenen, Greenville, Ohio

(New York Meeting, February, 1925)

If asked whether limestone production was a mining problem I would not hesitate to answer emphatically in the affirmative. The question, "When is a quarry a mine?" is familiar. The immediate mental picture induced by the thought of limestone production is that of an open quarry. All are familiar with the open pit in the iron-producing districts of Minnesota and Michigan and the open cuts of the so-called "porphyry" coppers of the West. If these are mines, they differ little from limestone quarries in general mode of operation; if quarries, why do they need the attention of mining engineers?

During 1923, the United States produced in round numbers 70,000,000 tons of iron ore. The limestone production of the United States for the same period was something over 100,000,000 tons. In tons, it about equals the oil production of the United States.

The uses of limestone are legion. A paper read by a prominent engineer of Chicago, at the meeting of the National Crushed Stone Association held last February in St. Louis says: "There is no industry in the United States today that is more basic in its operation or by itself controls more industries. There is hardly a chemical operation, hardly a metallurgical operation or building operation that a crushed-stone man does not control if he will jump in and make the full utilization of it." Some of the many uses are for road metal, concrete, railway ballast, building stone, riprap, and rubble, the manufacture of iron and steel, alkalies, calcium carbide, magnesia, carbolic and carbonic acids, asphalt filler, mineral wool, poultry grit, sulfuric acid, phosphates, nitrates, soap, baking powder, the purification of copper and prevention of coal-mine explosions, to say nothing of the quantities used in the making of lime and cement. It has been said that without iron we would revert to the Stone Age; how much iron would we have without limestone? From the point of view of the mining engineer, using the term in its broad sense to include geologists and metallurgists, the production of limestone is important because of its occurrence, volume, commercial importance, and the problems presented by its recovery and treatment.

The large limestone deposits situated on the surface and in close proximity to markets are becoming depleted; rapidly in some cases, more slowly in others. In the search for new deposits, the geologist is particularly interested. He can help not only as to actual location, but also in predetermining whether a given location will furnish stone suitable for the market it is intended to supply. Users of limestone are becoming more and more particular as to the chemical and physical properties of the stone they buy. Some limestones admirably suited for one market are useless in another. The manufacture of lime and cement as well as the use of flux stone might be termed the "metallurgy" of limestone. Lime is burned today in many places exactly as it was hundreds of years ago. Though cement manufacture is of more modern development, combustion engineers say the modern rotary kiln for cement making is not the last word in efficiency.

At a recent meeting of the Ohio Local Section, the effect of different grades of coal on the cost of steel manufacture was discussed and it was quite evident much saving could be made with certain kinds of coal. If the grade of coal is important, why would not different grades of limestone react similarly? At one quarry, two kinds of limestone are mined, one white and one gray or blue. It is stated that both have the same chemical composition and make equally good lime, except that the lime from the one is a little whiter. Something causes that difference in color. The gray limestone is hard while the white is soft. Other peculiarities in this material might offer interesting problems to the metallurgist.

To the mining engineer interested in production, limestone is important because of its volume, commercial importance and the problems presented by its recovery. Most of the limestone is produced from open quarries, of which there are three types, depending on whether the crushing plant is below, above, or on the same level as the quarry itself.

In the first type, the stone goes to the crusher by gravity, by an inclined tramway or by locomotives and cars. This can be compared to western copper mines and hillside quarries. In the second type are found the greatest number of both limestone quarries and open metal mines. Many limestone quarries are limited in their lateral extension by their location within city limits or other causes. Many metal mines, operating on wide lodes or massive deposits, or like the iron mines of Minnesota and Michigan, also belong to this type. In quarries within city limits, the mining engineer might develop a system of underground mining that will allow for lateral extension. By this means, heavy blasting, the greatest objection to city quarries, would be largely eliminated. Some system of delayed caving over weakened pillars, after exhausting the supply of stone from stopes, would seem to offer possibilities for study. In the third type, with quarry and crusher on the same level, are

a smaller number of open quarries as well as open metal mines. The reason is that limestone is exploited principally from horizontal beds, and progress is downward as well as lateral. Therefore quarries started in this way soon become of the second type, due to the lowering of the quarry floor. In all three types of open quarries, as in open mines, both single-face and multiple-bench methods are used. There are quarries operating in one face 240 ft. high and others 10 ft. high. Metal mines tend more to the use of several benches of moderate height. Many quarries are now standardizing on benches of 50 ft. vertical height, as being most economical for shovel operations.

Few open quarries or mines are free from the expense of overburden removal. Because of the comparatively higher value of its product, and its greater vertical extent, the metal mine can usually stand a greater cost per ton in this respect. On the other hand, smelting and refining charges against the metallic ore add materially to the ultimate unit cost and thus reduce the amount that can be allowed for stripping. Furthermore, the metallurgy of limestone or its calcination to lime or cement, paralleling the smelting of metallic ores, would automatically result in a higher market value for the ultimate product and likewise allow the removal of more overburden. The lime and cement manufacturers are turning to the so-called higher-cost mining methods.

Methods for removing overburden are practically the same, for both metal mines and quarries. Mechanical means, such as the steam, gas, or electric-driven shovel, dragline, cableway, and clamshell excavators are all in use, as is also pick, shovel, and wheelbarrow work, supplemented by drag scrapers and auto trucks.

Methods of blasting are the same. Electric, gas, steam, and air-driven well drills sink holes for the high benches, while machine drills, both piston and hammer, are used on the lower benches and for secondary blasting. Regarding explosives, there are probably as many different kinds used in quarrying as in mining. Recent experiments with liquid oxygen in quarries and in mines point to interesting possibilities of that explosive for both underground and open mining. In quarries as well as in mines, blast holes are sometimes charged with two different strengths of explosive.

The proportion of open metal mines using mechanical shovels for loading cars is greater than in limestone quarries, because they do not require a sized product. In many cases where the quarry uses hand methods, mechanical means would not apply as, for instance, the loading of stone for consumption in lime kilns. The kiln requirements for a sized stone prohibits the use of mechanical shovels, unless the cost and operation of screening machinery is less than the extra cost of hand loading and sorting.

Hauling from quarry or open mine to crusher is accomplished by identical means, including inclined tramways, overhead cableways, and gas, electric or steam locomotives, with end or side dump cars. Some limestone quarries use the fast rotary-dump cars, similar to those for coal mines.

The crushing of limestone does not require much different practice than the crushing of metallic ores. The tendency is toward larger and larger initial breakers, it being realized that it is cheaper to crush than to blast stone. While many limestone crushing and screening plants are well designed and operated, others are badly balanced and uneconomical. For example, as a result of the increased scarcity or high cost of labor, quarries that formerly used hand-loading methods have installed mechanical shovels without changing their crushing equipment. Others, when increasing their breakers, have not increased their secondary crushers and screening capacity. Here alone is a wide field for the mining engineer.

Underground mining of limestone is as yet of comparative minor importance. Nevertheless, as shown by my notes and observations of the past year, of the 100,000,000 tons of limestone produced in this country annually, something over 6,000,000 tons come from underground workings. Many cement and lime manufacturers have found it cheaper to mine than to remove overburden. Others find they can get a cleaner stone, and thereby a higher grade product, from the mine than from the quarry. Still others have turned to mining to solve the question of year-round production.

Methods of mining in use range from unsystematic, irregular breast stopes, through combinations of room-and-pillar mining with underhand and overhead stoping in flat deposits, to elaborate inclined and vertical shafts with back stoping over shrinkage in steeply pitching strata. In one mine limestone is being hoisted from a horizontal bed through a vertical shaft 550 ft. deep, and in another a vertical shaft 350 ft. deep is installed on the vertical side of the open quarry. But, thus far there are few instances of limestone being mined from shafts. It is generally extracted through tunnels or adits driven into the side of an abandoned quarry or the side of a hill. Here the methods of the metal and coal miner have been added to the quarryman's own ideas.

Room-and-pillar methods are almost universal in the limestone mines. Their applications are about as varied as the number of mines. Room-and-pillar methods are commonly termed tunnel mining, probably because they are usually begun as large tunnels driven from the side of a former open pit. These tunnels are carried from 8 to 18 ft. high in a single breast, and from 12 to 50 ft. wide. Pillars sometimes take the form of ribs, but are more often circular or square in section. Their size depends generally on the judgment of the operator, there being no set rule for

proportioning them with respect to the ground removed in the rooms. Long ribs are sometimes used to protect main haulageways, with square or round pillars in the rooms. Some operations are driven methodically on surveyed lines, with regular cross entries from room to room, while others apparently have never been seen by a surveyor.

Some tunnel headings are driven along the roof, followed by simultaneous bench stoping behind the drills; others reverse the process and carry the tunnel heading on the floor, followed by back stoping with upper holes. In one case both back and bench stoping are followed with a tunnel heading in the center of the stratum. In one or two instances, a central tunnel is driven the full height of the seam, followed by side holes to widen the room as required. Back stoping by upper holes in a metal mine, where the breaking is done directly over trammers, is not usually considered good practice because of the danger of leaving loose ground above, but in the limestone mine, where the holes can reach a good parting in the strata, this objection does not apply so forcibly. In an Ohio mine, the limestone stratum lies on an 8-in. bed of soft shale. Advantage is taken of this to use a coal cutter to undercut the limestone, after which it is blasted like coal. Various combinations of shrinkage stoping with tunnels are also employed where the thickness of strata warrants.

The placing of drill holes in limestone is at least as varied as in metal mining. For tunnel driving, drills range from the Jackhamer type held in the operator's hands to heavy piston drills mounted on 8 to 18-ft. columns. With the latter, miners work from the top of portable stages. Tripods are sometimes used to drive headings. At one plant, an ingenious contrivance enables the driller to continue operations without waiting for the shoveler to clean up the face. It consists of a car fitted with a counterweighted boom, operated with a hand winch. On the end of this boom is a steel cage. The driller mounts this cage and with a Jackhamer drills out the whole 30-ft. vertical face by using a bottom cut without lifters, while the muckers clean up the previous blast below him. Wedge cuts, either in the center or at one side of the room, are quite common. Sometimes the ground is broken in triangular blocks; in which case the holes are drilled as in the initial wedge cut, all meeting at the bottom of the wedge.

Whatever opinion may be held respecting limestone quarries in general, there can be no doubt that the underground limestone deposit is a mining problem. But, its problems differ from metal-mine practice in many particulars, and any metal-mine method used in limestone without careful preliminary study of existing conditions may cause serious trouble. Mining engineers have called it folly to think of carrying rooms over 30 ft. wide; on the other hand limestone operators hold there is no danger in rooms 100 ft. wide in limestone. There are instances

where both are wrong, and others where both might be right. However, a limestone mine that has had careful technical study and advice invariably shows it on the cost sheet. The American Lime & Stone Co. of Bellefonte, Pa., has one of the few underground limestone mines in this country operating on an inclined stratum, and using a regular back-stoping method over shrinkage and loading through chutes. That the company is successful indicates that limestone production is a mining problem.

In conclusion, I have found that very few limestone operations use the service of mining engineers. To the average quarryman any mining system spells expense, and it would surprise many of them to learn that so-called expensive limestone mines often produce stone at a lower cost than does the open pit. Mining engineers should, therefore, endeavor to convince the limestone operator that limestone production is a mining problem.

DISCUSSION

Oliver Bowles, New Brunswick, N. J.—I am so thoroughly convinced of the growing importance of underground work in the production of limestone that I had the author make a detailed study of limestone mining for the Bureau of Mines and prepare a report on the principles of limestone mining. Many limestone operators, long accustomed to open-pit work, are being forced to mining. About 6 months ago I thought there were twenty-five or thirty underground limestone operations in the United States but the author has been finding new ones until his list now runs nearer sixty. Some of these are very extensive; one at least has 4½ miles of underground workings.

There is an ever-expanding field for the engineer in the operation of limestone mines and quarries. Some of the larger companies realize the need of skilled engineering advice, but many of the companies regard the engineer as an unnecessary expense. Although almost every metal mine, even those handling only a few hundred tons of ore per month, employs a mining engineer, many limestone operations ten times as large employ no mining engineers. Few mining engineers are at all familiar with limestone operations, and few limestone producers have the advantage of mining engineering knowledge. This is a situation that demands correction.

J. T. Singewald, Baltimore, Md.—Where can the line of demarcation between cement rock and limestone quarries be drawn?

S. R. Russell, Wilmington, Del.—The natural cement quarries operated at Akron, N. Y., 50 or 60 years ago are all out of business now. The natural limestone quarries they speak of now have been abandoned. The other quarries are new and devoted to the manufacturing of Portland cement, lime, etc.

Engineering in Limestone Production

By C. C. Griggs,* Washington, D. C.

(New York Meeting, February, 1925)

From its inception, a limestone quarry or mine should be under the direction of a capable engineer. Before it becomes a reality, he should outline the future results, plan the most economical methods for moving the materials and the most efficient equipment, and pilot the undertaking along the narrow pathway of success, avoiding the pitfalls of uneconomical production and the precipitous walls of scanty profits. Inspection of successful limestone properties shows that all have had difficult engineering problems, the solution of which have required keen engineering ability.

In approaching a subject of this nature, it is logical to follow the progress of the limestone operation from its inception to the end, as reflecting the engineering required. There are four major divisions: Investigation, equipment, development, and operation.

Investigation

On the reliability of the engineer's estimates and the soundness of his judgment depend the success or failure of the enterprise. When one visits a prosperous concern, realizes that the limestone is of a constant chemical composition, sees the mechanical devices installed, and watches the output leave the plant in trains of railroad cars or fleets of vessels, he may overlook the fact that in the remote past this great creation was born in some man's brain and evolved through competent engineering.

Many factors must be considered before a promoter could procure the money necessary to launch such an enterprise, for a conservative banker will only recommend a successful producer while the promoter must provide funds on his own and his engineer's judgment. An engineering investigation must be made preliminary to expenditure for actual operation, which, for a limestone deposit, would naturally embrace such subjects as:

1. Tonnage available........	Readily available. Possibly available. Chemical analysis.

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2. Marketability of product, and effect and possibility of increased production during life of property.	Limestone flux. Cement. Building blocks. Chemical uses: Carbide, sugar, paper, alkalies. Fertilizer. Plaster and wall finish. Road material.
3. Costs..................	Operating: Repairs, quarrying, preparation of product, development (current). Overhead: Management, supervision, sales. Taxes, insurance, and interest.
4. Working conditions.......	Weather conditions in district and their possible effect upon full time operation, curtailed operation, and incidentally the transportation of product by rail or water. Labor.
5. Cost of plant and equipment.	Equipment necessary for quarrying, preparation of product and loading for transportation.
6. Physical difficulties.......	Water supply: Limited or unlimited. General operating: Obtaining supplies, obtaining repairs.
7. Selling price.............	Estimate made for product throughout life of quarry.

After compiling his data, as outlined, the engineer is ready to prepare his report. For a limestone property he must bear in mind that the industry depends on large production and small profits. As the small margin does not permit the use of such safety factors as are applicable to other minerals, all items must be given careful consideration before his decision is made. While the engineer may be too liberal and report favorably on a property not meriting such a forecast, he may also be too conservative; and as the margin is narrow, he may condemn a property that under proper management would prove an unqualified success. Satisfied as to three items: life of deposit, average production, and expected profit, the final answer is merely a matter of figures. Obviously a promoter should assure himself and his investors that the undertaking would return all the money required for plant, equipment, land, etc., as well as a fair rate of interest on the investment. Leading valuation engineers in America and England hold that the Hoskold's formula is satisfactory in meeting these conditions:

$$Pn = \frac{1}{\frac{r}{R^n - 1} + r'}$$

in which Pn = the present value of each \$1 operating profit accumulated during a life of n years, r' = interest rate on capital, r = interest rate for redemption, and

$$R^n = (1 + r)^n$$

One would not care to invest in a limestone property without assurance of at least 10 per cent. return and that at the end of the operations the company would have on hand the original investment in quarry, plant, and equipment, either to distribute as return of capital, or with which to purchase another property. The factors given below, when applied as will be shown, will do this. Only a few factors are given, for a 10 per cent. annual return on the investment, plus an amount which, placed in a sinking fund at 4 per cent. compound interest, will return the capital. The other factors for any period are readily available.

At 10 Per Cent. and 4 Per Cent.

Years Life		Years Life	
5	0.702675	25	0.322549
10	0.545581	30	0.282893
15	0.444619	35	0.251559
20	0.374302	40	0.226196

As an example, suppose the engineer has determined the following: Life of property, 30 yr.; expected profit per ton, 50 cents; annual production, 50,000 tons; estimated cost of plant and equipment $250,000. Then, expected profits would be: 30 × 50,000 × $0.50 = $750,000, and the present worth of this amount, which would produce the return stated, would be: $750,000 × 0.282893 = $212,169.75.

This indicates that the proposition would not justify a plant and equipment costing $250,000, for there would be nothing left with which to purchase quarry land, and provide for the other expenditures necessary at the beginning. If the estimated cost of plant and equipment required were $150,000 instead of the $250,000, it would prove a profitable venture, assuring the investors of a 10 per cent. return, if the cost of the quarry land, development and other initial expense did not exceed the difference of $62,169.75.

Many mines are killed by too much, or ill-advised, equipment. The estimate of the present worth of the earnings, as illustrated, furnishes a ready check on the amount justified for plant, equipment, and development; for, if these estimated initial expenses exceed the present worth of the expected earnings, it would be better to invest the money in safe securities than to take hazardous chances. As countless safe investments returning 6 or 7 per cent. interest may be obtained, the extra 3 or 4 per cent. would barely compensate for the chances taken in promoting an unproved enterprise.

Equipment

The choice of equipment is dependent on the engineer's ability and judgment. After determining his financial limits, an error in the selection or location of the various units may mean failure when the supreme test of operating comes. He has a wide range in choosing his equipment.

Numerous successful labor-saving devices are now available. The predetermined output of the quarry is the controlling factor. Whether the output shall be 50 tons per day, as sometimes occurs in limestone for burning, or thousands of tons, as in extensive enterprises, this factor must govern. Fig. 1 shows the smallest and the largest crushers used in limestone production. The small crusher (on the flywheel of the large one)

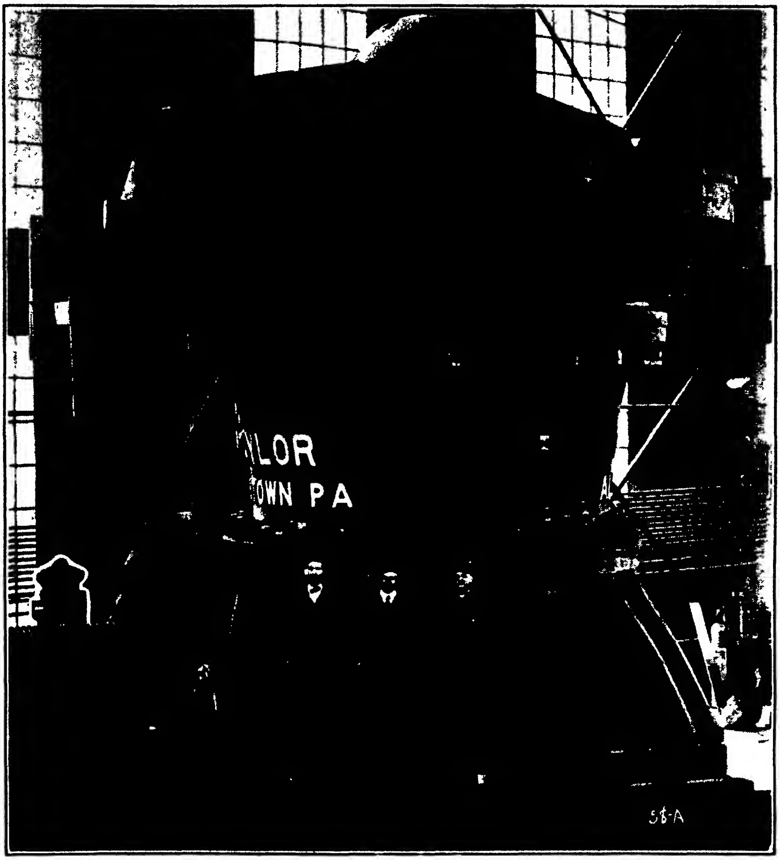

FIG. 1.—SMALLEST AND LARGEST CRUSHERS USED IN LIMESTONE PRODUCTION.

handles about 1 ton per hr. and has a 2½-in. opening; the large one handles 3000 tons per hr., with a 60-in. opening. Probably the largest steam shovel used by any limestone producer in the world has an 80-ft. boom, a 52-ft. dipper stick, and an 8-yd. dipper. The same company has recently added a shovel with a 70-ft. boom, a 48-ft. dipper stick and a 10-yd. dipper.

Many mechanical devices are available for handling the stone. A very complete plant is that of the Michigan Limestone and Chemical Co. at Rogers, Mich. All the illustrations in this paper are furnished through

the courtesy of the officers of that company: Carl D. Bradley, president and general manager, and C. B. Willard, assistant to the president.

Fig. 2 is a bird's eye view of the plant, harbor and equipment. From the time the rock is blasted in the quarry until it is unloaded from the

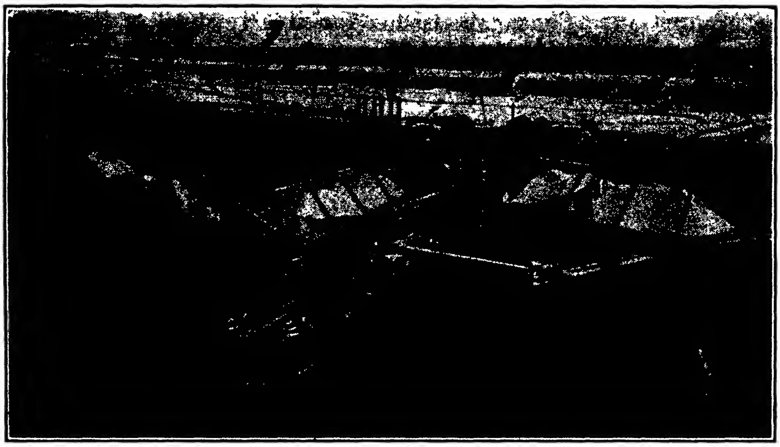

FIG. 2.—VIEW OF PLANT, HARBOR, AND EQUIPMENT AT ROGERS, MICH.

ore-carrying freighters of over 13,000 tons capacity, the handling of the stone is as nearly automatic as human engineering ability can devise. The limestone is loaded into cars, brought by locomotives in trainload lots to the automatic dump, where, after dumping, the empties pass on

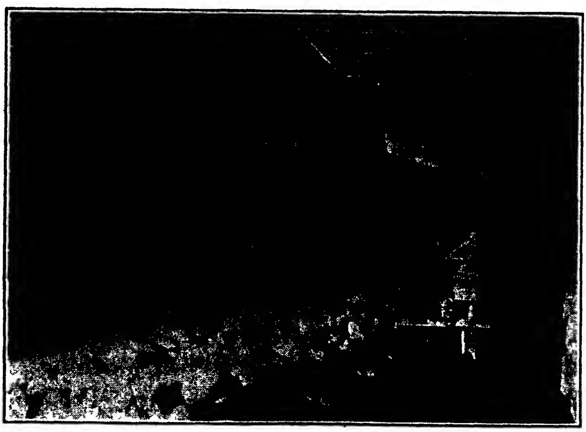

FIG. 3.—A TUNNEL GATE FROM STOCK PILE AND PART OF BELT CONVEYOR.

without switching back. The stone then goes to the large crushers, meeting a stream of water where it is thoroughly washed. The crusher product is screened into different sizes and distributed to stock piles by belt conveyors. Underneath the stock piles, other belt conveyors

FIG. 4.—FOUR CONVEYORS DISCHARGING SIMULTANEOUSLY INTO A FREIGHTER.

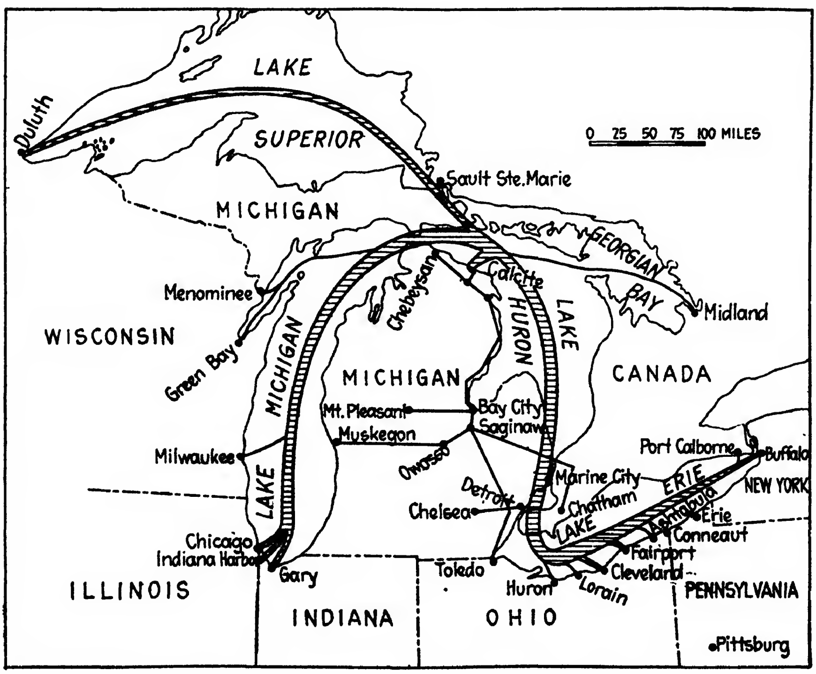

FIG. 5.—DISTRIBUTION OF LIMESTONE SHIPMENTS.

carry the limestone into openings in the top of the freighters. Even the freighters have hopper bottoms, which feed on to belt conveyors delivering the stone into an elevator for unloading on shore. Fig. 3 shows a tunnel gate from the stock pile and part of the belt conveyor. Fig. 4 shows four conveyors discharging simultaneously into the freighter. Fig. 5 illustrates the distribution of limestone shipments; especially interesting as showing the advantages of location. Although limestone is not always found where most desired, engineering ability will find a way to make it available at the points where needed. The distribution as indicated is ample evidence that this company has effectively solved its problem.

Development

Contemporaneous with the plans and selection of the plant and equipment must be the plans for development, so that when all units are installed the property will be in shape for production. Among other things, the following must be decided: Whether several small working faces should be provided at the quarry, or dependence be placed upon one large opening. Whether the tracks for the transportation of stone should be arranged parallel to the face of the quarry, or in fingers radiating from the main artery. Whether the overburden should be stripped extensively beyond the working face, with the problem of its disposal, or taken care of in the plant by washing.

Each plan has its own engineering problems, but the method and cost of the development are the important ones, for the development outlay becomes an initial capital expense and must be provided for before recovery is possible through sales of product.

Operation

Although the work is practically of a routine nature, engineering skill is as essential also throughout a successful operating career. Changes and additions are continually taking place; new plans in transportation, new markets, competition and new problems of every nature must be met.

DISCUSSION

W. C. Phalen, New York, N. Y. (written discussion).—It is quite generally conceded that first-class limestone properties, well located with respect to markets, are becoming scarcer. The farther afield industries must go for this commodity, the more expensive the transportation to points of consumption; these differences in cost must be made up, in part at least, by cutting cost of production by various means. Among the latter the employment of skilled engineering talent, at least in a consulting capacity at the outset, is the most obvious.

The conditions of distribution from fields on the Great Lakes are unique in that boats returning to the centers of limestone production generally carry coal; thus greatly reducing transportation charges.

Underground mining of limestone is engaging the attention of some producers and consumers. A very important industry on the Ohio River, where the surface supply of stone gave out entirely, was saved for years to come by turning to an underground supply, where the problem is essentially that of mining. Doubtless, examples of this kind could be multipled. It is of interest to note, from one of the papers submitted, that the proportion of stone mined to that quarried from the surface has reached 6 per cent. The stone so mined must represent a high-grade article.

When selecting properties for investigation and in their subsequent development and operation, the engineer or quarryman needs the services of the capable geologist, especially during the early stages of the work. Much valuable time and useless experiment may thus be saved. Over a wide range of territory in the Eastern States, first-class stone is quite restricted in its geologic occurrence. The experienced geologist knows where these horizons are located, and therefore where first to look or rather what territory to eliminate at the outset. In the selection of limestone for industrial purposes, and in studying marble deposits, the well balanced coöperation of geologist and engineer is just as important as in working a lead-zinc or copper deposit. The investor may well look to such coöperative work as a distinct economy in the long run.

JOHN RICE,* Easton, Pa.—This paper seems to deal entirely with the question of limestone production as contrasted to mineral deposits of all kinds, whether of chemical or of metallic value. The mineral aggregate used in the United States is probably about 200,000,000 or 300,000,000 tons a year, including limestone and stone for other purposes, but there is a large field of quarrying entirely aside from limestone proper. One very essential use is railroad ballast and road building, which have an enormous tonnage in this country.

One of the newest developments is the distribution by trucks, which is getting to be very important. One quarry of ours now handles about 600 tons a day by truck, in addition to its railroad distribution.

The selling price of crushed stone is much more of a problem than is the selling of flux because the units of sale are frequently smaller. The selling problem is not an engineering one but engineering phases materially enter into it, especially the screening of the product, recrushing unmarketable sizes, storage and recovering. There are few data regarding the problem of screening in the crushed-stone or any other

* President, The General Crushed Stone Co.

business, unless it be coal. Another feature, which may not be so applicable to limestone itself, is the disappearance of the market.

The average life of a quarry is more or less of an unknown quantity but, in relation to taxation, it has become a serious problem; we are still discussing with the Government the question of amortization in our 1917 tax report. Its representatives are back now for the fourth survey of our values, to determine whether we should depreciate our properties on the common-sense basis of the difference between the original cost and the salvage value and distribute that over the life of the operation or whether individual items of the capital account shall be depreciated according to an arbitrary scale, independent of the life of the operation. That is an engineering and accounting problem. Here the real problem is, how long is the operation going to last? The engineer can help to determine what is fair under those circumstances.

The arithmetical problems involved in the formula given are not clear to me. By making certain substitutions in that formula, I can get some relationship between the formula and the table on the opposite page. However, the question of determining how much of a plant investment is justified to the extent of going into the most minute considerations of compound interest, is not nearly as important nor as uncertain as the margin of profit which can be made if the investment is made. I am willing to take any engineer's report if he can guess within 10 per cent. of of the profit of the undertaking, as affected by operating costs and life, without worrying about the compound interest on the sinking fund. It is necessary to know what you can do with your investment after you get it. These refinements tend to discourage the practical men from considering the engineer's points of view.

SAMUEL M. SHALLCROSS,* Bellefonte, Pa.—I agree with that last statement. If an estimate is within 10 per cent., plus or minus, I consider it very good. There is very little opportunity for a mining engineer to become connected with a limestone plant, if he is a mining engineer only. Consultants are necessary at times and are employed quite extensively, but an engineer in the limestone industry must be not only a mining engineer, for those plants that have mines, but a high-grade mechanical engineer, electrical engineer, heat engineer, and chemist. It is a jack-of-all trades that meets our requirements to the greatest extent. The limestone industry has not progressed to the point where we can afford permanent high-grade specialists in the professions mentioned.

OLIVER BOWLES, New Brunswick, N. J.—In determining the profit or loss in any proposed limestone enterprise, one factor is usually less uncertain than in metallic orebodies, namely the extent and quality of

* General Manager, American Lime and Stone Co.

the orebody. Metallic ore-vein reserves are estimated, in a general way, from prospect drill holes, but there is always uncertainty through the danger of pinching out, the occurrence of barren rock in the veins, or other contingencies. The limestone orebody is usually a well-defined sedimentary bed of fairly uniform composition and uniform thickness. Thus, with a limited amount of prospect drilling, the operator may estimate with practical certainty the reserve tonnage of rock, which in this instance is the pay ore. At the mine of the American Lime and Stone Co. at Bellefonte, Pa., a limestone 98 per cent. pure lies in a bed 77 ft. thick dipping at an angle of 52° at the surface. This bed extends for miles with little variation either in thickness or in chemical composition, so that the ore reserve was known to a practical certainty before mining was begun.

How to determine the value of a limestone in place and the relation of this factor to other factors on which the success or failure of a limestone enterprise depends are points on which the author may be able to give further information.

Nathan C. Rockwood,* Chicago, Ill.—This paper gives a simple illustration of approximating the value of a limestone property, also a brief description of the largest limestone quarrying operation in the world. There is one vast difference between such mining operations as mining engineers are familiar with and a limestone, or any other, quarry operation. With limestone, one is not dealing with a material that has a fairly uniform value throughout the world, which is bought and sold through national and international exchanges; rather, he is dealing with something having a value that may vary from nothing to several dollars a ton, depending on how essential it is to some local industry.

It is the life of the market far more than the life of the deposit that determines the value of the deposit and the feasibility of developing it. The prospective producer of limestone must see with reasonable assurance a market within 200 miles of his plant and he is far less concerned as to whether his deposit will last than as to whether his market will last. In western New England there are many deposits of fine limestone, the principal use for which is in the manufacture of chemical lime used by paper mills, tanneries, and textile mills. We are safe in assuming that each and all of these industries have passed their peak in New England and are on the decline; therefore, the limestone deposits of New England will far outlast the life of only the industries they can serve with profit; and their present value may never be exceeded. When the paper mills, tanneries, and textile mills move to locations nearer sources of raw materials, limestone deposits of good enough quality to meet their needs will always be found nearby.

* Editor-Manager, *Rock Products*.

Again, a quarry may be developed and a crushing plant erected, at a cost of several hundred thousand dollars, to produce stone that it is estimated will be required to build a system of paved roads within a 150-mile radius of the plant. The road-building program may be limited to a life of 10 years; in which case 10 years is the only safe limit to the life of the quarry operation, for it may be so situated that it will not be able to reach any other market in competition with more favorably located plants.

The point of this discussion is that any consideration of a quarry development that does not place local market possibilities ahead of all other factors in the problem does not reach the real heart of the quarry industry either from an engineering or an economic point of view.

George Milliron,* West Winfield, Pa. (written discussion).—The first limestone mine in the United States was developed at West Winfield, Butler Co., Pa., in 1894. The mining of limestone was a radical departure from the accepted method of winning this material and experienced operators saw nothing but disaster in store for this new venture. To F. W. McKee, owner and operator of the limestone quarries at West Winfield at that time, is due the credit of originating the idea of mining limestone. He operated the mine in conjunction with his open quarries until 1899, when his limestone interests were taken over by A. G. Morris, under whose management more attention was given to the mining project. In 1902, the mine was producing 400 tons of limestone daily and in 1906 was producing 600 tons.

In 1910, Mr. Morris turned over his limestone interests at West Winfield to the Pittsburgh Limestone Co., which approached the mining problem with considerable caution. The operation of the West Winfield mine proved that limestone mining was practicable and possessed many advantageous operating features.

The limestone measure is known geologically as the Vanport Ferriferous. It is a flat-lying measure and varies in thickness from 10 to 22 ft. It is massive in formation and has well-defined horizontal cleavage.

From the small venture at West Winfield in 1894, eight mines have evolved with an annual production in excess of 2,000,000 gross tons of limestone; 90 per cent. of this tonnage is consumed by furnaces in the Pittsburgh district and the cement mill at Universal, Pa.

Most of the properties are operated under long-term leases on a royalty basis. The royalty paid the landowner varies from 1 to 2 cents per gross ton. An advance royalty of $1 per acre is paid until the tonnage mined from his property exceeds the accrued advanced royalty.

* General Superintendent, Limestone Mines, Pittsburgh Limestone Co.

The mining properties vary in size from 1000 to 3000 acres. The properties are surveyed and mapped. Diamond drilling, supplemented by churn drilling, tends to prove the chemical content and continuity of the limestone throughout the property. Elevations are taken on all outcrops, diamond- and churn-drill tests. From these data, the mine map is projected. Keeping in mind the life of the proposed mine, care is taken to secure grades favorable to haulage and drainage.

The original practice was to drive entries 40 ft. wide and rooms 60 to 80 ft. wide. This method required considerable timber to support the roof. Two main entries were driven parallel and cross entries were driven off right and left from main entries at 500-ft. intervals; 50-ft. pillars were left between main entries and the first room turned from cross entries. Present practice is to drive main entries 25 ft. wide and rooms 35 ft. wide. Main-entry pillars are carried 30 ft. wide and cross-entry and room pillars 20 ft. wide. This practice renders the use of timber almost negligible. About 4 ft. of limestone is left to form the roof. This is in two layers of limestone; the top layer is 28 in. and the bottom layer 20 in. thick. This thickness of the roof layers obtains where the entire measure has a thickness of 22 ft. Where the measure diminishes in thickness, the roof layers diminish in thickness proportionately.

When opening a mine, the outcrop stone is removed by open-quarry methods until the overburden has attained a height of 30 to 40 ft. The maximum overburden in this district is 325 ft.

Two methods of mining are in vogue. In hand loading, a 3-ft. bench is carried on the bottom of the measure, a 6-ft. breast stope, and a 4- to 8-ft. overhand stope. The varying thickness of the overhand stope is due to the varying thickness of the measure. The limestone is underlaid by shale. Where the overburden is heavy, the limestone does not part readily from the shale; the result is a rough floor to shovel on and the broken shale becomes mixed with the limestone, thereby increasing the silica content of the stone. This difficulty is obviated by leaving the 3-ft. bench. The bench is mined by drilling vertical holes. Where the loading is accomplished by power shovels, the entire measure is mined as a breast stope.

Waugh Model 21 and Ingersoll-Leyner No. 248 drills mounted on tripods are used in breast drilling, Jackhamer type drills are used for bench drilling, and Waugh and Ingersoll stopers are used for the overhand stope drilling. In breast drilling, the angle system of drilling is practiced. The maximum depth of hole drilled is 14 ft. Round hollow drill steel, 1¼ in., is used on the Waugh Model 21 and the Ingersoll-Leyner 248 with lugged shanks and four-point McClellan and hollow-center double-chisel bits. The starter bit is 2¼ in. diameter, with a 1⁄16-in. drop on 30-in. change. On the Jackhamer type drills for bench

and secondary drilling 7/8-in. hollow hexagon steel is used and 7/8-in. solid hexagon steel on the stopers. One foot of drilling is required to produce 1 ton of stone. Averages of 150 ft. per 9-hr. shift have been maintained by the Waugh Model 21 and the Ingersoll-Leyner No. 248.

Tests and practice have proved gelatin dynamite to be the best explosive for this class of mining; 30-, 40-, and 60-per cent. strengths are used. All primary blasts are detonated by No. 8 electric fuses. Where the mine is not wired for electricity, a hand-operated blasting machine is used; when mines are wired for electricity the current is used. Enclosed switches are provided for the various section of mine and are located 800 ft. from the working face. These are locked and so constructed that the door to the switch cannot be closed until contact with the firing line is broken. No. 14 solid-rubber covered wire is used for the blasting circuit. Joints are soldered and taped and porcelain insulators attached to wood supports inserted in holes drilled in the ribs support the wire. Secondary blasting is accomplished by the use of fuse and No. 8 blasting caps.

Hand loading is done on a contract basis at a fixed price per ton; two men are worked in a room. Hand loaders average 30 tons per 9-hr. shift. Osgood Model 21 and Marion Model 25 shovels driven by compressed air are used extensively in the various mines. The Osgood shovels are equipped with 3/4-yd. dippers and the Marion with 1-yd. dippers. The Marion shovels require 14 ft. of headroom and can operate in workings 25 ft. wide. The Osgood shovel, when fitted with a 12-ft. boom and a 6-ft. dipper stitch can operate in 12½ ft. headroom, but requires 25 ft. width to swing. The Osgood shovels have caterpillar traction and the Marion shovels wheel traction. The Osgood shovels average 400 tons per 9-hr. shift and the Marion shovels 600 tons per shift. The Osgood shovel requires one shovelman and one ground man; the Marion shovel requires one shovelman, one craneman, and one ground man. The shovels require 500 cu. ft. of free air per minute.

The standard track gage is 36 in.; main haulage roads are laid with 60-lb. rail and 6 in. by 8 in. by 5 ft. ties; 40-lb. rail and 4 in. by 6 in. by 5 ft. ties are used in the rooms. No. 4 turnouts are used on the main haulage and No. 3 turnouts on the room haulage. The mine cars are steel end-dump fitted with 18-in. wheels, 2½-in. round axles, 28-in. wheelbase, and have a live load capacity of 5 tons. Electric and gasoline mine locomotives are used on the main hauls, mules and small gasoline locomotives (3 to 4 tons capacity) gather the loads from the working faces to the main gathering stations. The gasoline locomotives in service on main haulage vary from 10 to 15 tons. Gasoline locomotives have the advantage that they can be installed more quickly and cheaply than electric locomotives; but they are more expensive in upkeep and breakdowns which interrupt production. To overcome production interruptions an extra

unit is necessary. The greatest objection is the contamination of the mine air by the obnoxious gases from the exhaust. The ideal mine haulage installation is electric trolley locomotive for main hauls and storage-battery or combination trolley and storage-battery locomotives for gathering.

Natural ventilation is generally relied on; and when the mine is operated on one shift only, no trouble is experienced. All primary blasting is done at the end of the shift, when all the miners are out of the mine except those in charge of the blasting. The interval between shifts gives the smoke and fumes from blasting ample time to dissipate. Two mines are ventilated mechanically. Considerable trouble is encountered in keeping the brattices in repair, because of the heavy concussion caused by the primary blasts.

Limestone mining is applicable to areas where the overburden is too heavy for profitable open quarry operation and the product must be free from material foreign to the measure. Mines possess a strong advantage over open quarries in that weather conditions do not interfere with production. The average temperature in a limestone mine is 55° and in severe winter weather the fluctuation will not exceed 5°.

Manganiferous Iron Ores of Cuyuna District, Minnesota

By Carl Zapffe,* Brainerd, Minn.

(New York Meeting, February, 1925)

A rise in less than ten years from obscurity into great prominence economically, tersely summarizes the history and status of the Cuyuna manganiferous iron ores.

The Cuyuna district produces and ships mostly high-phosphorus iron ore, but the annual production of manganiferous iron ore is increasing rapidly and productions from individual mines are becoming more regular and more dependable as to grades and tonnages. This ore bids fair to become, shortly, the principal product of the district and is responsible for its present economic prominence.

The iron ores of the district have been described, by the author and others, in many publications and will not be discussed here. Lately the manganiferous iron ores have been given some attention, but the range and variations of chemical composition of the ores, the principal physical characteristics of the ores and their deposits, the relative importance of the different ores and their possibilities in future developments, and the life of the respective reserves have not been discussed. It is impossible to give all of this information with the positiveness necessary for it to constitute a reliable guide for investment or even for future mine development. Each property and each party presents a special case and deserves critical consideration. We are dealing with special ores and always with a set of new conditions. Sufficient information of a general nature can be given, however, to indicate the reason for and the trend of the presently augmented developments in the district.

In a great thickness of a big variety of sedimentary rocks, probably of Upper Huronion age, prevailingly of green, schistose phases of slaty and volcanic material intricately intermixed, lies a thin bed containing lenses of iron-bearing formation. These lenses occur singly or in groups, thus causing the variation in the thickness of the formation; or they are separated at their ends and give rise to discontinuity or they overlap and display continuity with lateral offsets. Intense folding has added to the complications.

* Geologist, Northern Pacific Railway.

Generally a lens is tilted at a high angle and appears as a long single band. In a few places, these steeply dipping beds have been bent upward again and are pressed against themselves and duplicate the first beds in every respect; in other places the beds, though bent upward, are separated and the formation occurs at the rock surface in small rolls and then abruptly descends again as a single bed; or the bed may once have extended above the present surface but that part has long since been eroded and in its place appears now the green schistose rock that originally occurred underneath it. Folding, therefore, accounts mostly for the greater widths of formation.

Within these lenses of formation are the ore deposits, which are distinctly a secondary enrichment by meteoric waters, beginning at the rock surface and proceeding downward. The shapes of the deposits are determined largely by the shape of the inclosing lens of ore-bearing formation, wherefore the ore deposits tend to be long and narrow in the single lenses and broad and shallow in the flatter lenses. In recent years a few deposits, because a little wider than ordinarily and because the overlying glacial drift was not too deep and was easily removed, were developed as open-pit mines. Underground mines are the more numerous.

It may be concluded that during the time of deposition conditions must have been favorable for the formation of both iron carbonate and manganese carbonate, although not necessarily at the same time or in the same places, as is evidenced by the preponderance of manganiferous material in one territory to its exclusion in another, and the many different relationships where iron ore and manganiferous ore exist together. The opinion is becoming more prevalent that much of the manganiferous ore is a replacement of iron ore. The ores represent quite a variety of hydrous oxides.

The district is large in area and ore has been found in many places. At present, the manganiferous ores are being taken from the part known as the North Range, centering around Ironton, Riverton, Trommald, and Crosby.

Two Classes of Ore

The investigator must recognize at the outset that there are two kinds of manganiferous iron ores. The most important basis for a grouping is chemical composition, which determines different uses for the two kinds of ores. This division is easy to make because the ores are high or low in phosphorus and silica, and variable in the content of manganese and iron. In the deposits, the combinations are either high-phosphorus and low-silica or low-phosphorus and high-silica, the latter combination usually carrying the greater manganese content and the less moisture.

The ores may be grouped according to color. The Cuyuna ores are inherently a mixture of iron and manganese; the color suggests the probable content of the manganese, the color becoming darker and blacker as manganese increases. No "straight" manganese ore exists, barring specimen samples; Cuyuna ores are known as manganiferous iron ores and the unadulterated black color does not exist. Representative piles of ore range from brownish-black or greenish-black, for the low-phosphorus ore, to various shades of brown, for the high-phosphorus ore. The color is quite as determinative as is the chemical analysis and, for convenience, it is usual to speak of the ores as brown or black. The darker the color, the higher is the manganese content; and whereas the black ores are the better ores in this respect, it is more significant that black denotes low-phosphorus and high-silica.

To date, the black ores have always been found in narrow bands; the lenses are numerous but short and small tonnages are the rule. Most of the mines from which they were produced are now idle but the deposits have not been exhausted. Extraction has been, characteristically, by underground methods. On the other hand, the brown ores constitute deposits of large tonnage, are often associated with large quantities of iron ore, and generally are possible of extraction by open-pit methods. Although it is not accurate to say that the classification can be extended to embrace even the method of mining as a basis, the greater part of the brown ore is mined in open pits.

In the Cuyuna-Mille Lacs property is a well-defined layer of black ore in the midst of a large red and brown manganiferous formation. An underground mine was started in 1912; at first, the property was not developed for the purpose of extracting this black ore, but when the war was begun, in 1914, it immediately became the sole product. This was the first mine of its kind to attract attention; it became idle in 1919. In 1923, extensive drilling demonstrated the presence of much typical brown ore on another part of the property and showed possibilities for an open-pit operation. The production of black ore from the shaft and the old Cuyuna-Mille Lacs deposit may be at end and the production of brown ores from an open-pit may follow and predominate. The property has been renamed Louise. That represents the closest association of these two ores on a large scale on one property, but it is not a gradation of the two kinds of ore.

So far no intermediate class has been found. The Hopkins mine, operated for a short time in 1918, produced the two kinds of ore from two widely separated pockets; the ores were mixed when hoisted and mixed again when shipped, so that to one who has seen the ore in the cars or who may now examine only the cargo analyses, this may seem to be an incorrect statement. Somewhat similar situations have occurred elsewhere.

Even iron ore has been mixed with manganiferous ore, which obviously alters the appearance and the analyses.

Distribution of Ores in Deposits

The relative position of the black and brown ores with reference to the top or bottom of the ore-bearing formation, or in the main geological horizon, is open to debate. Much is conjectural and, from a practical standpoint, it may remain so.

In one small area the black ores predominate almost to the exclusion of the brown ores; while in a small area several miles away a little black ore occurs in the midst of much brown ore.

The brown ores are distributed throughout the presently productive part of the district. They have been mined, for the most part, from deposits that also contain iron ore. In only a few of the reliable mines has the ore produced been prevailingly the manganiferous iron ore. Some mines gained prominence from the production of manganiferous ore when, in fact, iron ore was the principal product; or were it not for the iron ore in the deposit, a large mining operation would have been impossible. The large reserve tonnage of brown ore in several mines would justify considering those mines primarily for their manganiferous ores.

In some iron ore mines, like the Meacham and Armour No. 1, the associated manganiferous ore is persistently along the foot wall; in others, like the Huntington, it is along the hanging wall; while in still others, like the Armour No. 2 and Hillcrest, it occurs in the midst of the deposit. Each property is a special case. To classify as to distribution is of little economic value. What, with little development, in the early days was considered an erratic or irregular occurrence is substantiated today, as well as magnified, by the greater development.

Periods of Dominance of Black and Brown Ores

Each class of ore has been dominant at certain times. The first shipment of manganiferous iron ore was made in 1913; it amounted to 24,434 tons and was used in an experimental way and in small lots. In 1914, the European war excluded importations of manganese ores and alloys that had been dependable for decades. Furnace operators demanded substitutes approximating the usual foreign supplies and found the Cuyuna black ores the nearest to these. Under the stress of the times, the increased demand for iron and steel and the consequent industrial expansion, many black-ore properties were developed. This, in turn, created a larger output from the existing mines, brought into being many underground operations, and brought black-ore deposits into prominence.

With the close of the war, these low-phosphorus ore substitutes were no longer desired, so the mines were shut down. Although these ores were produced and accepted under periods of stress and were rejected when the situation changed, they gave impetus to new ideas among consumers of ore, and the use of manganiferous iron ores in every-day furnace practice and the making of high-manganese pig iron became established facts. But since 1919, the adoption of the practice apparently was based on the condition that the ores should be low in silica content, available in large quantities, produced with regularity, and with little or no variation in composition, for that is the present status at the producing mines. That excluded the black ores and opened the field widely for the brown ores.

Since that date, the development of open-pit mines on brown-ore deposits and the production from established underground iron-ore mines where these brown ores are abundant have progressed with increasing speed. It will require another season or two before the present known properties or mines will be developed to their best operating possibilities, and because of the greatly increased demand for these ores the annual production of manganiferous iron ores will exceed the annual production of the ordinary Cuyuna iron ores.

Production

Production figures have been variously reported because of the different classifications made by statisticians regarding the content of manganese that constitutes the division between iron ores and manganiferous iron ores. According to a division made on the basis that these ores were produced separately and used specially (and not according to a division made on a basis of setting up some arbitrary content of manganese), the production for the Cuyuna district totals 4,735,806 tons as of Dec. 31, 1923; the greatest annual total production was 963,853 tons, in 1918.

Actual production of black ore ceased in 1918, but the accumulated ores at the mines were gradually acquired in the following years and, in 1923, the last of such old ores was shipped from the stock pile at the Cuyuna-Mille Lacs mine. If more such ore is desired, idle or abandoned mines must be restored or new ones developed. The total quantity of black ore shipped was 1,121,373 tons.

The production of brown ore began early by necessity of removal and not because of use for the ore; for instance, in the Armour No. 2 mine, an established iron ore mine, some brown ore was encountered with the iron ore and had to be taken out but it was not shipped immediately. The ore was not desired, but substantial shipments were made in 1916 and have continued each year since. For the district, a big slump occurred

in 1919, 1920, and 1921, but shipments increased greatly in 1922 and 1923. Judging by the parties using these ores and the open-pit developments now in progress, resulting from the growing demand for this ore, if business conditions in the industry had remained good, it is not unlikely that the 1924 shipment of this ore would have approximated 1,200,000 tons. At the present writing, perhaps not over 700,000 tons will be shipped.

Chemical Composition

An idea of the composition of these ores may be obtained by examining published analyses, either those recorded in ore sales books of selling agencies or those in the annual publications of the Lake Superior Iron Ore Association. To illustrate the compositions and variations, a few analyses, representing different years and different deposits, are presented in Tables 1 and 2 for some properties that may be deemed typical.

Table 1.—*Season Analyses Typifying Various Black Ores*

	Iron (Dry), Per Cent.	Phosphorus, Per Cent.	Silica, Per Cent.	Manganese, Per Cent.	Alumina, Per Cent.	Moisture, Per Cent.
Algoma	32	0.07–0.09	20–23	17–19	2–3	7– 9
Clarke	35.5	0.104	15.28	16.95		
Clarke	35	0.058	23.86	10.99		
Cuyuna-Mille Lacs	37	0.09–0.10	18–20	11–12		13–14
Cuyuna-Mille Lacs	36.73	0.106	12.93	17.44		13.48
Cuyuna-Mille Lacs	37.46	0.106	7.97	22.01		13.50
Ferro	29–32	0.07–0.09	17–19	20–21		7–10
Gloria	28	0.18	17–19	17–18		8– 9
Hopkins (black ore, expected analysis in 1919)	38	0.063	16.45	16.03	1.73	9.91
Mangan No. 1, crude	36	0.13	22	13	2.50	9–10
Mangan No. 1, hand picked	33	0.13	17	17	2.50	9–10

The moisture content for brown ores is notably variable, more so than is indicated by the analyses in Table 2. These ores might be divided into high- and low-moisture ores. Not uncommonly brown ores mined from deposits that are primarily operated for their iron ore show the lower moisture contents; such ores also are invariably lower in alumina. The manganiferous ores from the Mahnomen pit were crushed and washed in 1923, thereby reducing the alumina and moisture contents; but in 1924 the ores were only crushed. The ores from the Sagamore pit, probably the wettest ores now mined, are dried to reduce the moisture;

TABLE 2.—*Season Analyses Typifying Various Brown Ores*

	Iron (Dry), Per Cent.	Phosphorus, Per Cent.	Silica, Per Cent.	Manganese, Per Cent.	Alumina, Per Cent.	Moisture, Per Cent.
Arko	41	0.290	9	10–12	4	14–15
Armour, No. 2	46–49	0.18–0.21	8.5–9.5	5.2–8.2	3.5–4.5	11–13
Hillcrest	46–49	0.25–0.28	6–9	4–6	3.8–4	8.5–9.5
Huntington	53.65	0.309	7.29	2.78	2.92	9.56
Milford	43.05	0.238	6.70	11.41	4.00	18.00
Martin	52.81	0.182	7.60	5.04		13.50
Mahnomen	50.14	0.277	6.97	4.93	3.24	12[a]
Mahnomen	46.80	0.283	5.48	8.25	4.20	12[a]
Mahnomen	43.33	0.297	5.10	11.72	3.25	12[a]
Mahnomen	41.03	0.296	4.43	13.89	3.25	12[a]
Mahnomen	36.42	0.310	3.90	18.69	3.20	12[a]
Sagamore	43.00	0.280	5.00	10.00	5.00	10[b]
Sagamore	48.00	0.280	8.00	6.50	4.00	10[b]
Sagamore	51.00	0.280	8.00	5.00	4.00	10[b]
Sagamore	53.50	0.280	8.00	3.50	3.50	10[b]
Sultana	38	0.174	9–10	13.75	3.50	15.00
Portsmouth	46.20	0.286	6.44	6.32	4.52	17.00
Portsmouth	43.22	0.298	6.33	9.55	4.84	17.00
Armour, No. 2	46.88	0.201	10.43	7.21	4.07	11.31
Louise	45.95	0.213	8.72	8.98	2.98	14.00

[a] Washed ores, 1923.
[b] Dried ores, expected analyses for 1924.

compared with ores from other mines the dry alumina content is high. The conditions suggest a close relationship between high alumina and high moisture. A sintering plant has been erected on the Oberg-Evergreen property to treat brown ores that will be obtained from that property in 1925. In 1924, a small tonnage of manganiferous ore from the Wearne pit was used and a sinter produced that has an excellent physical structure. Sintering drives out all the water and burns up the material usually reported as "loss by ignition." Every effort is being made in the district to give the trade a desirable product.

The black ores are low in alumina and moisture and frequently are lumpy. The black ores mined have shown much impregnated vein quartz, and hand-picking was always undertaken when these ores were mined; in addition, the ores are associated and intermingled with a parent rock containing iron silicates that contribute much of the silica. Some of these ores show a greenish cast because of that leaner material. Because of this intimate association of the silica with the iron and the manganese, it will be impossible to apply at the mine any known process of separation that will reduce the silica content.

It seems that for a while the trade will have to adapt itself to the use of the brown ores quite as they are known today, which may be said to have an average composition of 41 to 46 per cent. iron, 0.25 to 0.3 per cent. phosphorus, 4.50 to 9 per cent. silica, 5 to 12 per cent. manganese, and 3 to 4.5 per cent. alumina, excluding special grading to meet rare requirements. The average manganese content of all ores shipped will approximate 8 to 10 per cent. There is a tendency now to produce two grades, an 8 and a 10 per cent. If higher manganese is desired, some of the brown-ore mines can produce small tonnages. If lower phosphorus is desired, recourse must be had to a deposit of high-silica (black) ore; as these ores are costly to produce, their production will be deferred for some years.

Reserves and Future Possibilities

Most of the drilling in the Cuyuna district was conducted vigorously in the earliest years; since then few properties have been subjected to intensive exploration. In that earlier period, manganiferous ore was deemed undesirable and drills were placed to avoid it. Many properties are known to contain some manganiferous ores. The present tendency is to strengthen known or developed properties by extending the mine developments, and by acquiring adjoining parcels and increasing the magnitude of the existing operation. Another reason for not developing new tonnages, in later years, was to avoid creating burdensome taxation for idle properties. For that reason it is better to wait until the ore is desired and then test the possibilities of the numerous prospects.

Lack of explorations makes it impossible to formulate tonnages accurately for the entire field. The production record of mines that produced black ores shows a very small average annual output per mine. There are about a dozen properties that could be developed or restored. The average production for each of a number would hardly exceed 50,000 tons per year, because of the small sizes of the known deposits, and a few would not be much more than a clean-up scram. From a standpoint of reserves, they may be estimated to be the equivalent of about one-eighth of the brown-ore reserves.

The brown-ore deposits now being operated are in a state of development suitable for accurate estimating. They are generally well known, and are of a magnitude that enables a fairly close estimate to be made of the tonnage where explorations are perhaps inadequate. The largest producers ship, on an average, several hundred thousand tons per year; the smallest 50,000 to 100,000 tons; and others about 150,000 tons. Had the early prediction of production of 1,200,000 tons for 1924 been fulfilled, the average shipment this year for all mines would have been between 150,000 and 200,000 tons. The maximum annual production

of the Mahnomen mine has almost reached 400,000 tons. The Sagamore mine has been studied by various careful investigators, and it is the opinion of the author that, including all ores, all present consumers of Cuyuna manganiferous ores can be supplied from this one mine for many years. This mine has not been operated to capacity nor is it fully developed; it could produce over 4000 tons per day and easily deliver 700,000 tons per year.

Obviously the future will bring with it a greater consumption of these ores, as it has done in all important lines in the industry. Such demand will be met by a greater development of new tonnages. Consumers may become less exacting in their requirements, especially when the only available supplies of a raw product are not always up to desired requirements, as we understand them today. Without trying to see too far into the future, the conclusion seems inescapable that after making due allowance for increases in consumption and analytical requirements, consumers are amply protected for fifteen years at least with suitable ores produced in large amounts and at reasonable costs. This does not mean that the Cuyuna ores will be exhausted at that time, but the rapid comprehensive changes that now take place in a few years in the iron and steel industry hardly warrant our seeking further into the future of a commodity, like manganiferous iron ore, that is just making headway. Such ores undoubtedly will be available and will be mined for thirty years or more, but the guarantees required and costs may differ, explorations may bring to light new ores, different mixing may be resorted to, and by other practices the life of the deposits extended materially; for such a time our present standards cannot form a reliable guide.

The reserves of iron ore in the Lake Superior region are known quite well, and at a stipulated rate of consumption the approximate life of the reserves can be estimated. Each year new material will be made available. Twenty years from now ores high in silica will be used, either in crude form or after having been subjected to some beneficiating process. Every such effort will add greatly to the available reserve tonnage and extend the life beyond our first calculation.

The Cuyuna district possesses more manganiferous iron ores than all the rest of the country; but although required in smaller amounts than iron ores the supply is not so great that it will outlast our iron ore resources. The reserves of manganiferous iron ores in the Cuyuna district are not as well known as they should be. In many areas, the presence of such ores, where not mined now, are indicated either by holes that were drilled in search for iron ore or by abandoned shafts started during the war. The demand for high-manganese low-phosphorus ores during the war and for low-silica high-phosphorus ores since the war has created a sort of stalemate for the one ore and an unprecedented rush in production for the other, and explorations are halted.

Everything relating to the brown ores is momentarily a standard of measurement for comparison, and that is not sufficient for purposes involving the future.

Manganiferous pig iron is a special pig iron. The alloy ferromanganese contains about 80 per cent. manganese; spiegeleisen contains about 20 per cent. (16 per cent. during the war); and manganiferous pig iron may be said to contain between 4 and 10 per cent. No alloy can be made unless the proper relation between manganese and iron exists in the ore; therefore, after allowing for the heavy losses of manganese in smelting ores, like Cuyuna ores, containing from 8 to 10 per cent. manganese on the average, are usable only for making high-manganese pig iron. Manganiferous pig iron cannot be used instead of ferromanganese or spiegeleisen.

The use of manganiferous pig iron is rapidly gaining favor and it appears to be one of the most important recent advances in metallurgy where the raw products are involved. Undoubtedly increased adoption of the practice, rather than retardation, will be the rule. The assured increase in reserves of iron ore will be of greater proportion than increases in reserves of Cuyuna manganiferous iron ores if only such kinds as are now classed as available reserves are taken into consideration. A plausible conclusion is that the present reserves of such manganiferous ores are not big enough for the requirements of the Lake Superior reserves of iron ore likely to be available twenty years hence.

That conclusion is faulty because the comparison is between an ore that is well investigated and with suitable beneficiation established and an ore that is without either. For the iron ores we allow tremendous increases in tonnage as the result of beneficiation; but for the manganiferous ores no allowance is made for changes in practices, nor is exploration of properties as complete as for the iron ores.

Reference has been made herein regarding an ore intermediate between the brown and black ores, and the statement was made that none was known. There is a third class, however; it constitutes the material rejected today because too high in silica. The eventual necessity of resorting to high-silica manganiferous ores will become just as urgent as in the case of iron ore. Because the black ores are usually associated with large widths of siliceous manganiferous formation, conditions are favorable for the development of large open pits on it and enable low mining costs to be obtained. The ore produced, if we may call it that, will be higher in manganese than is the present brown ore. Also, that material will be low in phosphorus, alumina, and moisture. In silica it will range between 25 and 35 per cent. Iron and manganese combined will total about 40 to 45 per cent. dry. In one place alone there is enough such material in a continuous band, for a mile or more, to produce a tonnage far in excess of any maximum figures now producible for black and brown ore

reserves combined. There are other big areas. To some people it may seem absurd to refer to or consider material so high in silica, but it is the use of manganese and a growing practice that are under consideration and twenty years hence something must be offered to replace the rapidly depleted brown ores. Due to low-cost mining and the higher manganese content this material will not be shunned. It will offer new problems, but they will be met. This material will have an advantage in contributing more manganese per ton than do the brown ores now being taken eagerly.

As a matter of good conservation practice, even now some black ores might be mined and absorbed with the brown ores shipped and thereby consumed in suitable mixtures before mining and absorbing them becomes less favorable, except as they may in time become parts of open-pit deposits of the high-silica ores just described.

The Cuyuna district will never rival the Mesabi district from the standpoint of tonnage, nor are manganiferous ores needed in the same large amounts as are iron ores, but the Cuyuna district is destined to become, in a relative sense, as important and essential to the industry for its manganiferous iron ores as the Mesabi district has become noteworthy for its preponderance of open-pit low-phosphorus iron ores.

DISCUSSION

A. K. Knickerbocker,* Virginia, Minn. (written discussion).—The author makes a broad distinction between the "black" ores (the higher silica, higher manganese, lower phosphorus, lower alumina, and lower moisture ores), and the "brown" ores, or ores with exactly opposite characteristics. In a broad way, this color distinction does hold. The brown ores are usually limonitic in character and tend to the characteristic brown limonitic color. The blacker ores derive their color from their increased content of the black manganese oxides; but these colors are not entirely indicative. The brown ores vary in color from blackish-brown, to brown, red, and purple, with all their intermediate shades, and a similar variance obtains in the black ores. Black denotes high-manganese, not necessarily either low phosphorus or high silica. In some orebodies, the blacker the ore the lower is the silica, which in these ores exceeding the ordinary content is usually introduced by crisscrossed and narrow veins of pure quartz or by a film or matrix of low-grade, siliceous, low-manganese ore, of a brownish red which surrounds the varying sized lumps of hard, low-silica, high-manganese very black ore.

The author states that no intermediate class of ore has been found, and mentions the Cuyuna Mille-Lacs mine, which has been renamed Louise. In this property there are three distinct orebodies, the northern of which is "black" ore, the southern "brown" ore; the middle has char-

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acteristics in alumina, silica, manganese, phosphorus, and moisure intermediate between those of the two orebodies mentioned by the author.

The paper may convey the general impression that the preponderance in use of the brown ores since the close of the war is due entirely to the superior quality of these ores. Nowhere has been brought out, in a sufficiently outstanding manner, that the real reason for the supremacy of these ores is a lower cost of production. The brown ores, in the mines from which production is now coming, lie in such a way that they may be attacked by open-pit methods; or they occur with iron ores in established underground mines operated primarily for their iron content. The black ores so far have been mined by strictly underground methods, for themselves only. If the operating conditions of the orebodies were reversed, it is reasonable to suppose the black ores would have continued to hold the supremacy. The development of open pits on brown orebodies toward the end of and immediately following the war, forced all of the underground mines to close, regardless of whether the ore was brown or black. That they will reopen in the future is beyond question; the probable date of such reopening depends entirely on the approaching of exhaustion of open-pit brown ores.

Certain it is that if black ores are to be produced in the near future, no such silica content as was shipped during the war, as shown by Table 1, can be shipped, except in special cases. During the war, because of the extreme demand for manganese and a corresponding disregard for other elements, mining in at least some of the properties was not confined to the orebody itself but extended into the surrounding formation, at all points where the formation carried a high manganese content. This is thoroughly proved on one property, the underground maps showing slicing to have been carried far beyond the bounds of the orebody as determined by the mine's own analysis maps.

The author assumes a great deal when he states that production of black ores at the old Cuyuna Mille-Lacs mine (now the Louise) "may be at end." This mine has been producing steadily ever since it was reopened in June, 1924. There is no sign that its production is at end. In mining the black ores on this property, the operators are working with the idea of staying within the orebody, and letting the high-manganese, high-silica, manganiferous formation remain until the rather indefinite date prophesied by the author. Analyses of shipments of the black ore from this mine, in 1924, are given in Table 3 to show the character of black ore now produced by this property.

Manganiferous ores are being bought for their manganese content. That an ore such as the above is more valuable to the purchaser than the average brown ore is evidenced by his willingness to pay more for it. He is buying a certain number of tons of metallic manganese, not ore, and because of the lessened number of tons of ore required to furnish the

TABLE 3.—*Analysis of Shipments of Black Ore from Louise Mine in 1924*

	Dried at 212° F. Per Cent.
Iron	37.02–38.01
Phosphorus	0.058–0.081
Silica	11.33–10.46
Manganese	19.89–17.58
Moisture	11.55–12.66
Combined metals	56.91–55.59

metallic manganese necessary, effects a saving on freights, handling charges, etc. Taking into account the increased value of these black ores, the character and size of the orebody will determine whether or not these ores can be produced by underground methods at a cost to compete with the lower grade brown ores.

Because of the insistent demand for a higher general manganese content, the black ores have not only a value in themselves—they are invaluable for mixing with the brown ores. Their high-manganese content increases the general manganese tenor, and as their characteristics in all other elements, including moisture, are opposed to those of the brown ore, their mixing with the brown ores presents nothing whatever that is not of value or of help to the resultant mixture.

CARL ZAPFFE (author's reply to discussion).—The purpose of the paper, primarily, was to tell about the reserves and the indicated future of all the Cuyuna manganiferous iron ores; but to present that information in a manner valuable to all interested parties, it was necessary to explain first the general situation as to these ores, present and past operations, and then to show wherein current adverse opinions about the characteristics of these ores and their extent had found an origin. Mr. Knickerbocker is interested primarily in the Louise mine, which is only a detail in the whole picture, and the points he raises are not exactly appropriate in a general treatment.

He states that some black ores (like brown ores generally) are low in silica. Such black ores are, however, insufficient in quantity to constitute a separate and profitable operation or to sustain an industry; therefore, they cannot be considered as of value in establishing a general rule when we know definitely that the big bulk of the black ore is high in silica. We know also that brown ores high in silica are refused by consumers; but as the bulk of brown ores is low in silica, they are chosen in preference to the black ores, although the ores are generally lower in manganese. No ore, regardless of manganese content or cheapness of mining, would be mined if the silica were objectionably high.

It is not true that the low cost of production is the sole factor determining the present choice between brown and black ores. The Portsmouth mine is a pit operation on brown ores and should be a low-cost

operation, but it has not produced ore for several years; on the other hand, the Milford mine is an underground operation and is producing heavily, but no iron ore is produced. The Hopkins mine is an underground operation and produces only manganiferous ore. The Sagamore is an open-pit operation in brown ores, but it has not produced heavily.

No mine operates exclusively today on black ores. The Louise mine is both an underground mine and an open pit. Recently the underground part has been restored in activity and is producing primarily black ore as low in silica as such ore permits, and it is adjacent to some marketable iron ore; the open pit is separate therefrom, is just being developed, and is on a very large tonnage of brown and iron ore. Between the two deposits of manganiferous ores, the bulk of the formation is material of a chemical combination not suitable as an ore today, regardless of name applied or method of mining; it is similar to an abundance of reserve manganiferous formation for which this district is distinctive. I considered it as belonging to the third class named and as constituting a future reserve. If it can be mixed with other ores produced from the present mine and formed into a desirable chemical composition, it becomes immediately available. Such is true of any reserve ore, and so does not alter the general situation.

While certain small tonnages of black ore are being sold, this is because the high-manganese content is desired to fill a special need at some furnace and, as intimated, undoubtedly a higher price is paid for it. The quantity taken is small, but that, too, does not alter the general situation; when such ore is needed it will be produced. But it is the low-silica brown ore that makes the Cuyuna district distinctive, and it is the low silica in the ore that induces consumers today to buy it in large quantities.

Economics of the Cuyuna Manganiferous Iron Ores

By C. P. McCormack,* Cleveland, Ohio

(New York Meeting, February, 1925)

The Cuyuna manganiferous iron ores can be a principal source of manganese for the iron and steel industry in the United States, provided metallurgical methods as a whole are adjusted so as to use run-of-mine ore. The use of manganese in steelmaking is growing. Increasing amounts of impurities in raw materials call for more manganese, a constant cheap supply of which is wanted.

There are few deposits of ore in the United States carrying over 35 per cent. manganese that can be mined and marketed at a profit in normal times. We are largely dependent on foreign ores. The small domestic deposits should rightly be held in reserve for an emergency, such as a war, when importation might cease. Even the production from lean ores, concentrated it may be, might not carry us through a protracted stringency.

The Cuyuna district is, therefore, during normal times capable of supplying a large total of manganese. The ores are iron ores containing 5 to 25 per cent. of manganese with the inverse range of 52 to 28 per cent. of iron. The manganese costs no more per unit in the ore than the iron, because cost of mining, largely by open-pit methods, is not affected by the manganese content. The manganese units should, perhaps, command a higher price, but as their value is contingent on metallurgical practice, a higher price may be justified only when a shortage in manganese occurs.

Manganiferous iron ores can never entirely supplant straight manganese ores though methods are employed that will permit them to do so partly. For the manufacture of ferromanganese, ores carrying above 42 per cent. manganese are needed. Ores with manganese running between 20 and 42 per cent. are used for making spiegeleisen. But established practice in certain plants, based on the admixture of manganiferous iron ores to straight iron ores has greatly lessened the consumption of high-priced, scarce, manganese alloys with good results.

The substitution of manganiferous ores for ferro and spiegel affects the manufacture of basic iron and its conversion into basic open-hearth

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steel. Successful replacement is a matter of adaptability, results, and costs. Cuyuna ores are not suitable for malleable and foundry irons, which have low manganese specifications.

Two classes of ore are produced, analyses of which are here given. They are the basis for this discussion.

	High-phosphorus Low-silica (Brown Ores)	Low-phosphorus High-silica (Black Ores)
Crude tonnage	28,000,000	3,500,000
Dry iron, per cent	42.00	31.00
Dry phosphorus, per cent	0.25	0.08
Dry silica, per cent	7.00	17.00
Dry alumina, per cent	4.00	2.00
Dry manganese, per cent	9.00	20.00
Moisture, per cent	13.00	10.00

The above tonnages are approximate, as all the deposits have not been thoroughly explored or developed. But they are on the conservative side and close enough to base future probabilities upon. They represent amounts of ore profitable to mine during average times and could be increased at inflated prices.

The high-phosphorus, low-silica class is involved mainly in the problem of substitution for ferro and spiegel. The low-phosphorus, high-silica class has its greatest possibilities in the substitution for manganese ores in the manufacture of spiegeleisen. Its utilization is of secondary importance to that of the first class.

Manganese contained in the two classes of ore is as follows:

	Tons of Manganese	Tons Manganese Allowing for 30 Per Cent. Smelting Loss
High-phosphorus, low-silica	2,200,000	1,540,000
Low-phosphorus, high-silicia	630,000	441,000
Totals	2,830,000	1,981,000

Note.—In addition to these classes, there is a third type (high-silica) that is greater in tonnage than the others combined. Its analysis would be roughly as follows: Iron, 16 to 20 per cent.; phosphorus, 0.075 per cent.; silica, 25 to 35 per cent.; alumina, 2 per cent.; manganese, 22 to 28 per cent.; moisture, low. This ore has no market now and is wholly undeveloped; its possibilities will be considered later on.

Assuming that 13 lb. of manganese is required per ton of basic steel and that 25 per cent. of this can be supplied by these ores, the above quantities of metallic manganese would supply the industry for 30 years at an annual steel production of 40,000,000 tons. Assuming that 25 per cent. of an annual iron ore production of 60,000,000 tons from the Lake Superior district requires a 10 per cent. admixture of these ores, the foregoing reserves of high-phosphorus, low-silica ore would last 20 years.

Before the expiration of these periods new ore supplies may be developed and deposits now unprofitable may become valuable ores, with metallurgical processes modified to suit. Therefore, a 30-year life would be a probable minimum synchronizing with the exhaustion of the present merchantable iron ores in the Lake Superior district. The reserves, then, are large enough to warrant full and serious consideration of the economics of this type of ore.

Function of Manganese

Manganese is the only desulfurizing, deoxidizing, and conditioning agent now known that can be profitably used. When not present in the raw ore, in sufficient quantity, it must be added either as ferro, spiegel, or scrap to the furnace burden or as ferro or spiegel to the hot metal —either before charging to the open hearth or at the finish. Approximately 70 per cent. of the manganese in the ore goes into the iron and is so utilized in the various stages up to finishing the steel. The only manganese addition then needed would be to bring the content in the tapped steel up to specification.

When present in sufficient amount within the blast furnace, manganese will combine with the greater part of any sulfur that is present, forming manganese sulfide. Much of this goes into the slag while a portion of the balance is transformed, either in the furnace or in the ladle, to Mn and SO_2; the SO_2 going off as a gas and the manganese returning in part to the iron, the remainder entering the slag as oxide. This desulfurizing action is maintained in much the same way within the open-hearth furnace. It requires above 1 per cent. manganese in the iron to take up any appreciable amount of sulfur.

Manganese has a greater affinity for oxygen than has iron and will remove oxygen from iron or prevent its oxidation. This action is carried on within the open hearth when any manganese is present in the metal. Between 1 and 2 per cent. in the crude iron will give a residual amount of manganese in the bath varying between 0.25 per cent. and 0.38 per cent. depending on the carbon content, sulfur introduced by the fuel, and time of heat. The rest of the manganese enters the slag and equilibrium tends to be set up between that in the slag and that in the metal. Manganese, reduced by carbon from its oxide in the slag, returns to the metal, attacking any ferrous oxides present, after which a part goes back into the slag as an oxide. Manganese evenly disseminated through the iron is more efficient than ferro in pieces and there is less recarbonization to be done at the end. It is less wasteful than manganese ore charged in with the iron to the hearth.

Manganese gives a more even textured pig iron and, when not above 2 per cent. tends to soften the iron counteracting the hardening tendency of sulfur, while carbon is kept in the combined form.

Manganiferous Iron

Impurities in materials for steelmaking continually increase. Higher sulfur in coke ordinarily calls for a highly calcareous or increased slag volume in the blast furnace with slower driving and increased fuel consumption, which may be obviated, however, by putting in the iron about 2 per cent. manganese. Some progressive plants produce irons with between 1 and 2 per cent., but the practice is not general. A blast furnace making basic iron will operate better on 2 per cent. manganese than on 1 per cent., because of the fluidity of the slag and its wide desulfurizing action. The amount of slag required is diminished and it can be worked leaner thus permitting faster driving and less coke consumption. No deleterious effect is noticeable on the furnace linings. Low-sulfur iron is made for use in the open hearth. High silica in the ores must be neutralized by a base, otherwise it occasions heavy loss of manganese, which then acts as a base entering the acid slag, and some is lost by increased volatilization. Increased alumina content in ores tends to correct this and an increased amount of dolomite (except where the alumina is very high) will neutralize any further excess of acid.

Carrying the manganese higher than 2 per cent. in basic conversion iron is of questionable value. It is not allowable in cast iron and is uncontrollable on remelting in the cupola. Above 2 per cent. manganese, the blast furnace costs rise and the tonnage is lessened. The beneficial results obtained do not counterbalance these disadvantages. All manganese in the iron except for the 0.25 to 0.38 per cent. residual is lost in the open hearth, and therefore must not be thrown away when results do not warrant it. Some auxiliary process such as the electric furnace, taken up in more detail later on, may aid in establishing the use of iron carrying above 2 per cent. manganese.

Iron carrying 2 per cent. manganese is in a conditioned state and shortens the finishing period of open-hearth steel because of its action on the sulfur, introduced in the fuel. For every 0.25 per cent. of manganese above 1 per cent. in the charge, the production is ordinarily increased by 1 per cent. Also, in the manufacture of steel under usual conditions, manganese addition in the ladle to meet the steel specification is lessened at the rate of 0.7 lb. of metallic manganese (in either ferro or spiegel) for each $\frac{1}{4}$ per cent. of manganese above 1 per cent. and up to 2.5 per cent. in the charged iron. High residual manganese obtained from a manganiferous iron ore, will therefore save ferro and compared with a low residual, lower the cost of finished steel.

Manganiferous iron tends to give most steels better chemical and physical properties. Sulfur is cut down to 0.035 per cent. and ductility both hot and cold improved. Less trimming is required and mill yield is increased.

Adaptability of These Ores

The cost is usually the prime consideration. The manganese in the Cuyuna ores can be marketed at the going prices of iron; therefore the cost of reduced manganese up to 2 per cent. approximates the cost of an equal amount of reduced iron, so that up to that content these ores are a cheaper source of manganese than either ferro or spiegel. For example, when using an average iron ore carrying a low manganese (0.50 per cent.), it would take 49 lb. of manganese in the form of ferro, spiegel, or manganiferous iron ore to yield a ton of iron with 2 per cent. manganese. Allowing for 30 per cent. loss of manganese it would require 62 lb. of ferro or 251 lb. of spiegel, or 552 lb. of 9 per cent. manganiferous iron ore to supply the necessary manganese. Basing costs on the 1924 average and allowing for the iron recovery from these materials with their respective reduction costs, it is estimated that the comparative costs of the 49 lb. of manganese would be as follows: ferromanganese, $2.54; spiegeleisen, $1.99; Cuyuna manganiferous iron ore, $1.43. This same ratio of cost would hold true in whatever percentage of mixture is required. This latter is cheaper and, because its manganese is distributed through a greater bulk, it is more efficacious.

The phosphorus in the high-phosphorus, low-silica class, which is the adaptable ore for mixing purposes and constitutes the bulk of the reserves, is of no great disadvantage in basic iron, especially when only 10 to 15 per cent. is required as an admixture. Progressive producers, to save freight, are drying their ores, though high moisture in itself is of no fundamental consequence. The relatively few deposits of fine ores will not be worked until it is economical to agglomerate them; the other ores are as good in structure as the iron ores with which they would be mixed.

As the manganese is for purely medicinal purposes, it is necessary that the blast furnace be assured of a uniform manganese content in its ore mixture. A 10,000-ton lot may average 9 per cent. manganese while in blocks of 25 tons the manganese may vary from 5 to 15 per cent. Suitable mixing is therefore needed to prevent undue fluctuations in the manganese content of the crude iron.

Because of ununiformity of small deposits, many former operators have ceased work, the larger ones now being able to supply fairly uniform run-of-mine ore. The establishment of a number of grades to suit the fancy of the purchaser is impractical as it tends to raise the mining costs, thereby making a large number of mines or portions of mines unprofitable. It confuses the market; it does not build up confidence in the ores, and does not give to the metallurgist a stable starting point for new practice. The majority of the mines are now producing run-of-mine ore, which must be the foundation for continuous furnace practice and means a

stable cheap production from the Cuyuna range. It is then strictly up to the ore producer to maintain an even manganese content according to his guarantee of run-of-mine ore.

For basic-iron production, the high-phosphorus, low-silica ores are adequate and important. The needs for it, if fully developed, will absorb a normal production. Its phosphorus unfits it for making spiegel, though a preliminary smelting in a basic electric furnace might make it suitable. Even then only the best of the ores could be used, otherwise the cost of stepping up the manganese would be prohibitive.

The low-phosphorus, high-silica class is not now in demand and its utilization is dependent on metallurgical practice to be developed. The phosphorus is only relatively low and the ore is still in the non-bessemer class. To date the demand for ores containing above 28 per cent. silica amounts to about 2 per cent. of the total from the Lake Superior district, and has remained at this figure for the past 10 years. As the ores depreciate in iron year by year, the silica content goes up with the alumina, so that in the total ore consumed the total silica required seems to be automatically adjusted. High silica is needed only in smelting certain individual ores and under certain smelting conditions. Increased supplies of magnetic concentrates, and this applies especially to any future Canadian production, will develop some increase in demand for siliceous ores as admixtures. If manganese is required at the same time with silica, it would seem that the low-phosphorus, high-silica Cuyuna ores would be ideal. However, this condition would not be standard and would call for exact balancing of the manganese and silica, else too high a manganese iron would be produced because this class of ore carries relatively high manganese. Therefore, its probable application is in the mixing with high-phosphorus, low-silica ores, in order to give a higher manganese to the run-of-mine ore. It may also prove suitable for making spiegel.

Before going into the matter of spiegeleisen, the third class of ore will be considered. It is lean ore with 25 to 35 per cent. silica, and high manganese but with low iron. The tonnage is large but almost wholly undeveloped because of no market. It is excluded from the admixture use because of its too high silica. Its impurities and low ratio of iron to manganese eliminate it from the spiegel class. Some, as yet undeveloped, beneficiation process to remove the silica might make it available for any use. Some future method for smelting siliceous ores at a much lower cost than at present would make available these several millions of tons of metallic manganese. This future is indicated by the gradually increasing silica content in all of our iron ores, and can well be awaited as this class of ore represents but a small fraction of the invested capital in the other two classes and can therefore be held in reserve at a low cost.

Ordinary spiegeleisen requires low-phosphorus ores. It could be made from the low-phosphorus, high-silica ores for use in basic processes

except that the high silica would mean high costs. High silica causes a large loss of manganese, both in the slag and by volatilization, and greatly increased smelting costs because of the large slag volume necessary to carry off the silica, increased coke consumption, slow time of smelting, and heavy lining expense. The product would be a silico-spiegel as a considerable amount of silica would be reduced. Such an alloy may be made economically in the future in the electric furnace from this type of ore, or even standard spiegel. The silica could be slagged off in an acid-lined electric furnace without undue loss of manganese since, because there is no blast, very little manganese oxide would be formed, which would act as a base and go into the acid slag. Cheap transportation to and from centers of cheap electricity from developed water power will do much in this direction.

The ratio of iron to manganese in the low-phosphorus, high-silica class is under 2.50, which is the limit for ores for spiegel. The amount of silico-spiegel used is very small; mostly in the recarbonization of basic silicon steels and for special alloy steels. Increased use of silico-spiegel, and thereby of this class of ore, depends largely on future metallurgical developments. Therefore until new uses arise or the electric furnace is perfected with cheaper power, the best market for the low-phosphorus, high-silica class is in grading up quantities of high-phosphorus, low-silica ores deficient in manganese or else in supplying the demand for admixture to ores deficient both in manganese and silica, such as magnetic concentrates. With sulfur-bearing iron ores, it could be used as an admixture when the cost of the manganese is less than any preliminary treatment to remove the excess of sulfur from the ore. The reserves of the ore are small and they occur in separate lenses, so that any present lack of market for it will not restrain full production from the other class.

The making of manganese pig (5 to 20 per cent. manganese) is entirely possible except that the costs of reduction are high. When made, it is neither fish, fowl, nor beast. It may be substituted for certain amounts of spiegel additions when abnormal conditions warrant it. Such additions require presmelting, when the manganese content is uncontrollable and liable to heavy loss. Its manganese content is lost in the open hearth, therefore its beneficial results here must outweigh the cost of its manganese units above 2 per cent. It is too bulky to be used as a substitute for ferro as an addition at the finishing point of steel.

If electric smelting is ultimately developed, it will be possible to treat the slags both from the blast furnace and the open hearth and recover the manganese therein. This would favor the making of, say 10 per cent. manganese iron for conversion, thus obtaining high efficiency in deoxidization and desulfurization yet not losing this amount of manganese.

Experiments by individuals and the Bureau of Mines in the making of sponge iron may open new fields. One of the great difficulties in

utilizing sponge iron in the open hearth is its rapid oxidization due to its finely divided and porous form. Sponge iron made from a manganiferous iron ore and carrying high manganese would not so oxidize. It remains, therefore, for a process to be developed to recover the manganese from the open-hearth slag, thereby pointing a way in this direction.

Beneficiating experiments along mechanical lines on the Cuyuna manganiferous iron ores in the hope of increasing the manganese, and at the same time the iron, by removal of the silica, have to date been unsuccessful. The silica, in the form of iron and manganese silicates, is so intimately and chemically associated that the problem is extremely difficult. But this does not end the possibilities of concentration. The spread between the costs of beneficiation and the value of the concentrate has been based on the selling price of iron ore. A chemical or combination of chemical and mechanical methods may be profitable when the product is projected into the manganese-ore class. Such treatment of the ores would be in the endeavor to create new manganese ores and thereby conserve the raw materials necessary for ferro and spiegel. When the partial conservation of manganese can be acquired by using ores as they stand and at the same time make manganese available at a lower cost, beneficiation is not imperative.

Cuyuna ores are produced from a well-established mining district with developed extraction methods, transportation and dockage facilities and with as low freight rates to eastern consuming centers as the iron ores from the Lake Superior region. Well-organized and stable mining companies with long experience in iron mining have now entered the field and can supply manganese in large amounts at low cost to consumers needing or desiring this metal.

Metallurgical developments will open new uses for such ores, of which the supply is ample. The ultimate consumer who must gain or lose by any sufficiency or stringency can be assured that both ends are working—sometimes harmoniously, sometimes in spite of each other—toward conservation of our meager resources of manganese ore by wider utilization of these manganiferous iron ores.

DISCUSSION

T. L. Joseph,* Minneapolis, Minn.—I agree with the author as to the benefits derived from the use of manganiferous ores, but in view of our limited resources, I question whether this will prove the most efficient way of using the small amount of manganese reserves. In the blast furnace the benefits derived from manganese are due to indirect causes, it acts as a sort of medicine and helps to get rid of sulfur. In the open hearth, it cuts down the time of the heat and is beneficial in several ways.

* Metallurgist, Bureau of Mines.

However, there is a possibility of working out a means of concentrating the manganiferous ores in such a way that it will be possible to produce, perhaps, a low-grade ferro. There are certain low-grade ores on the Cuyuna, which perhaps could never be used to produce spiegel or ferro. These could be used according to present methods.

Joseph W. Richards, a number of years ago, suggested using these low-grade ores in the production of ferromanganese by running them through the blast furnace, slagging off as much of the manganese as possible, then putting this slag through a blast furnace using it as an artificial ore to produce an alloy approximating ferromanganese. At the Minneapolis station, we have been working on this problem and have succeeded, in a preliminary way at least, in separating the iron and manganese, recovering the manganese in the form of a slag that contains iron and manganese in such a ratio that it could be used to produce ferromanganese; of course most of the iron is recovered in the form of steel. I think the manganiferous iron ores of the Cuyuna will have a greater potential value if this line of development can be worked out.

J. Wilbur Van Evera,* Crosby, Minn.—The statement that there is a great deal of high-silica manganiferous ore on the Cuyuna Range that will probably be beneficiated may be questioned. As a general proposition, the siliceous manganiferous ores do not present as simple a problem in concentration as do the iron ores.

In 1923, the latest year for which we have complete statistics, there was shipped from the Lake Superior district a little over 2,000,000 tons of manganiferous ore averaging 6 per cent. natural silica, and a little over 1,000,000 tons of ore averaging 29 per cent. natural silica. The total shipment for that year averaged 7.32 per cent. natural silica. The low-silica iron ore and the low-silica manganiferous ore shipped were able to absorb over 1,000,000 tons of very high-silica ore.

These siliceous and these manganiferous ores are generally used as medicine in the blast furnace. It is desirable to have them separate, because of the greater flexibility in charging; but considerable of the manganese and the silica could be taken together.

The fight to reduce the silica in all ores that go into a blast furnace will be never ending, but the cost of separating silica from the high-silica manganiferous Cuyuna ores will be greater than the furnaces will be willing to pay, and after the exhaustion of the present supply of low-silica manganiferous ores, the furnace will take a large part of its siliceous and manganiferous ores together, in the form of siliceous manganiferous ore.

C. P. Perin,† New York, N. Y.—We are now dependent on India and Brazil for our manganese. In the British Empire, the principle is

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† Consulting Engineer.

growing daily to limit the use of their materials in other countries; and we are going to pay dearly for any manganese that comes from India. A contract with the Soviet Government is not worth anything; and in case of war between Russia and any other country, which would lead to the blocking of the Black Sea, no ore would come from that source. The recently discovered deposits in Mesopotamia are without transportation facilities; besides, they would come under the plan of the British Empire to retain the raw materials it possesses. We have got to look to some place like the Cuyuna range for our future manganese supply.

T. T. READ,* Washington, D. C.—The point has been raised in some of this discussion that the use of manganese ores in the blast furnace is uneconomic; that with our limited supplies of manganese it should be reserved for use in the open hearth. The Lake Superior district iron ores are running as high in silica as the blast furnace requires I believe and the problem for the future is how to use high-silica ore without running the pig-iron cost too high. Using more fuel to melt more slag in a blast furnace produces a vicious circle because using more coke to melt that slag brings in more sulfur and you must add more silica to make more slag to take care of the sulfur. There are some instances where siliceous additions are needed for a blast-furnace burden, but the average blast furnace in America is well supplied with silica.

L. E. IVES,† Cleveland, Ohio (written discussion).—The writer does not agree with the statements concerning the price at which these ores might be sold. The cost of producing manganiferous ore is generally higher than the cost of producing the usual standard iron ores of the Lake Superior district. In the first place, the actual cost per ton is generally due to physical conditions, which involve higher exploration costs, higher stripping ratio, and more lean ore to be removed, as well as considerable rock excavation required in benching down the steeply inclined sides of the open pits and, for underground ore, higher costs due to narrower and more irregular lenses of minable ore, and more or less selective mining. In addition, the combined metallic content of manganiferous ore is substantially less than the average iron ores produced in the Lake Superior district. So that based solely on the cost of production, manganiferous ore should sell at a higher price per unit of metallic content than straight iron ores; the benefits derived from the use of these manganiferous iron ores, however, amply justifies the slight additional cost. The statement that malleable and foundry irons have such low-manganese specifications that the use of manganiferous ores is eliminated, is hardly true. Some foundry-iron specifications call for quite high manganese and the tendency is toward the use of foundry iron containing higher manganese.

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† Sales Manager, Clement Quinn & Co.

The paper claims that present developed reserves of manganiferous ore are sufficient to supply the iron and steel industry for 20 years, assuming that the rate of consumption will continue to be the same. It does not seem likely that the rate of iron and steel production will continue the same for the next 20 years; from past records we should expect a substantial increase in production, even if the rate of increase should be very much less than it has been for the past decade. Besides, the rate of increase in the consumption of manganiferous ore has been substantial in the past few years, with nothing in sight at the present time to indicate any decrease in this rate. The present developed reserves, therefore, are not sufficient to last twenty years, but exploration will be necessary in order to develop the reserves that the industry should have.

The paper seems to give the impression that the use of manganiferous ores by blast furnaces is not firmly established. This is not the case. The practice of using manganiferous ores at the blast furnaces is well established, and there are comparatively few steelworks, at least, that are not already using such ores quite extensively.

The statement that manganese is the only desulfurizing, deoxidizing, and conditioning agent now known that can be profitably used, is not exactly true; aluminum, titanium, and vanadium are used for some of the conditions he mentions a little further on. Manganese, however, is generally recognized as the cheapest addition. The point is brought up that when present in a sufficient amount within the furnace, manganese will readily combine with the greater part of any sulfur which is present within reasonable limits to form manganese sulfide, much of which goes into the slag, while the balance oxidizes either in the furnace or in the ladle. How can manganese oxidize in a blast furnace in which the process is distinctly a reducing one?

An open-hearth authority in the Middle West, who has conducted numerous and lengthy experiments in the use of high-manganese iron in the open-hearth furnace, has determined that a manganese content between 1 and 2 per cent., in the basic iron, will increase the open-hearth production at the rate of approximately 1 per cent. for each 25 points of manganese in the iron. In other words, if with 1 per cent. manganese, the open-hearth production is 100 per cent.; with 1.25 per cent. manganese, the production will be 101 per cent.; and with 2 per cent. manganese, the production will be 104 per cent. It is not thought worth while to have the manganese run higher than 2 per cent., although manganese somewhat higher obtained at no expense would have no effect in the ordinary open-hearth practice. The increase in the open-hearth production is due to the fact that basic iron made with a relatively high manganese is in a more refined condition when delivered to the open-hearth furnace and, on account of the influence of the manganese on the sulfur of the steel the delay in the finishing period of the open-hearth

heat is avoided, or at least diminished. These figures are based on the average blast-furnace and open-hearth conditions. If the blast-furnace conditions are very ununiform and the fuel used in the open hearth is of more than the average sulfur content, the higher manganese in the iron will have a greater influence; and the reverse is true where the blast-furnace and fuel conditions are better than the average.

At a very large plant in the Middle West it has been demonstrated that high manganese in basic iron produces better open-hearth steel. Careful records have been kept in the manufacture of over 4000 open-hearth heats. The improvement in the steel is in both the chemical and the physical properties. Whereas the sulfur in the steel averaged 0.041 per cent. with iron of 1.15 per cent. manganese, the sulfur decreased to approximately 0.032 when using iron with 1.90 per cent. manganese. Neither do the plate-mill preliminary rejections tell the complete story; all the steel made with high-manganese iron is much more ductile and of superior quality in every way compared with that made with lower manganese iron.

It is of considerable economic interest, also, to note that the use of such high-manganese iron in the open-hearth process decreased the consumption of ferromanganese necessary to obtain the specified manganese in the finished steel. It has been found that with an iron containing 1.25 per cent. manganese, the residual manganese in the bath was 0.05 per cent.; with 1.75 per cent. manganese in the iron, the residual manganese is increased to 0.22 per cent.; and with 2.25 per cent. manganese in the iron, it became 0.27 per cent. It is therefore evident that to obtain 0.45 per cent. manganese in the finished steel, 60 per cent. more ferromanganese is necessary with 1.25 per cent. manganese in the iron, than with 2.25 per cent.

Steel Making in Alabama

By James Bowron,* Birmingham, Ala.

(Birmingham Meeting, October, 1924)

Considering the importance of the steel trade and the strategic position occupied in it by the Birmingham district, it may be surprising to many to learn that the first pig iron smelted with coke was made in Alabama on Feb. 28, 1876, although merchant pig iron had been produced in Rockwood, Tenn., in 1867—a plant that is still in operation

The heavy deposit of Clinton ore, extending from Pennsylvania into Alabama, varies greatly in accessibility, on account of geological changes such as erosion or anticlinal upthrow; it varies equally as much in thickness and in quality. The brown ores extensively scattered through the South also vary materially in quality—some are relatively low in phosphorus and high in manganese, and vice versa. The red ore varies materially in phosphorus, but the iron produced from this ore was always considered too high in phosphorus for treatment by the acid bessemer or open-hearth process and did not contain sufficient phosphorus for the basic bessemer process. Under these conditions there remained only the basic open hearth as a possible process; and for many years it appeared impossible to use this, because, with coke smelted iron, the silicon was too high to permit its use in basic lined furnaces.

Various attempts were made, from time to time, to produce a low-silicon iron, by carrying high lime burdens together with harder blowing, but the blast furnaces of the South were not equipped with the blowing power of today and from 3½ to 5-lb. pressure was the normal working condition. The result of these experiments, therefore, was that a furnace would get a lime set or be hastily changed to avoid scaffolding, and engineers and superintendents were careful not to renew the experiments. After the development of the beds of dolomitic stone in East Birmingham, the carrying of sufficient lime to bring down the silicon in the blast furnace to the permissible open-hearth limit was successfully done at the Alice furnace in Birmingham, commencing July 22, 1895. In a very short time the entire output of that furnace was being sold to different Northern steel manufacturers, with a guarantee that silicon and phosphorus should run below 1 per cent.

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* Chairman of the Board of Directors of the Gulf States Steel Co.

It is not to be supposed that the iron makers of the South had been vegetating in the meantime or content to be shut out from the manufacture of steel. To the writer's knowledge, there were at least twenty-one different efforts to make steel, in either Tennessee or Alabama, within the last half century; all resulted in laboratory success, but commercial failure. The Roane Iron Co. attempted to make bessemer steel, in Chattanooga, by bringing ore from North Carolina. That orebody was thin and the expense of mining and the freight to Chattanooga were too high to permit successful operation; besides some parts of that or of other ore used as a mixture were so high in phosphorus that rails broke when being thrown from the car during unloading. The experiment was not successful commercially and the plant was broken up and sold, but before this took place another experiment was tried there of much greater importance that lead to permanent results.

First Successful Steel Made in 1890

The Southern Iron Co., aided by officials of the Tennessee Coal, Iron & Railroad Co., manufactured a most excellent quality of steel in the year 1890 from 800 tons of iron made for them by the Tennessee Coal, Iron & Railroad Co. at South Pittsburgh. This iron contained less than 1 per cent. silicon, and 0.6 per cent. sulfur, and about 1.4 per cent. phosphorous. The steel bars produced were bent, hammered, and twisted cold, giving remarkable results. This steel was made by Mr. Talbot, who at that time developed the Talbot continuous process, afterwards so extensively used at the Pencoyd Works of Messrs. Roberts, now the plant of the American Bridge Co., and which has become one of the established methods of producing steel, but has not since been used in the South.

In Birmingham, experiments on a small scale had been made by the Henderson Steel Co., using fluorspar as a flux; later the Tennessee Coal, Iron & Railroad Co. leased, the plant then standing idle, and conducted experiments with Birmingham pig. The results obtained were sufficiently satisfactory to insure that successful operation was only a question of providing the necessary equipment on a sufficiently large scale and experienced management.

No one in the South engaged in the iron trade at that time had any money to spare. The iron producers sold their pig iron at a little more, and sometimes a little less, than the cost of production, to consumers in every part of the United States, and indeed to practically every foreign country where pig iron was used. The richest and most accessible ores and best coking coals were being used up and plants were being worn out with no provision for amortization of their costs and the industry was slowly losing out—or under the best conditions, marking time. There was nothing to warrant northern capitalists in putting money into the South for the production of steel.

The Birmingham Rolling Mill Co. undertook to produce steel by the basic open hearth on what it deemed a commercial scale, but which was not. On July 24, 1897, the first cast was made of bottom poured ingots weighing about 1400 lb. each. The furnace had been constructed largely as the result of a contribution of about $75,000 by public-spirited citizens of the city. The proposition was nothing more than experimental and the company failed in 1899.

Before that occurred, however, M. H. Smith, president of the Louisville & Nashville Railroad, tried to have the Tennessee Coal, Iron & Railroad Co. begin the manufacture of steel on an adequate scale. The country at that time was industrially paralyzed by the sequence of the free silver panic of 1893, the Debs railroad strike and coal miners' strike concurrently in 1894, the Venezuela-British war scare of 1895, the renewed free silver panic of 1896, and the shadow of the impending Spanish-American war of 1897–8. The operations of the district were almost stopped for lack of outlet for the pig iron, a semblance of activity only being preserved by the development of foreign trade which in the course of a single year grew to nearly 200,000 tons per annum—pig iron being shipped cheaply from southern cotton ports as ballast in cotton steamers to Europe. Under these conditions President Smith stated that the district was practically "broke" and that the only salvation was the production of steel on a large scale to give an outlet for the pig iron. This plea was rejected by the Executive Committee of the Tennessee Coal, Iron & Railroad Co. on the ground that no money was available for such a purpose; but the officers were authorized to subscribe $100,000 to the Birmingham Rolling Mill Co., payable over one year in pig iron and coal, and to contract with them that for a period of the years the company would itself not embark in steel as a competitor. But at its next meeting, the Executive Committee rescinded its action and instructed its officers to build the works and find the money for that purpose. The officers, first, made personal subscriptions for this purpose, then raised a similar amount from the citizens, and then had the Louisville & Nashville and Southern Railroads furnish an equal sum. This plan worked out well. It was examined and highly approved by Wellman, Seaver & Co. of Cleveland, Ohio, and their plans, in turn, were checked by Mr. Hunt of Chicago; the solicitation of funds among the directors of the Tennessee Coal, Iron & Railroad Co. was then begun. It was the writer's task to show them, one by one, that as the company was then producing on a large scale basic pig iron used by such companies as Carnegie Steel Co., Illinois Steel Co., and others, the same steel could be produced in Birmingham if similar furnaces were built and similar men were employed to handle them, and the freight on the pig iron to Pittsburgh or Chicago and the freight on the resultant product back to Birmingham would be saved to the railroads and other customers. The

money was raised and the works were started on the scale of 300 tons per day, producing 18 by 20-in. ingots.

Simultaneously with the construction of the plant, which was located at Ensley, Chicago interests were induced to build a rod and wire mill on abutting ground given for the purpose, the billets being carried over by conveyor from the Tennessee company's blooming mill to the rod mill. Accustomed to Chicago practice based on bessemer billets, the Alabama Steel & Wire Co. management had considerable difficulty in using the softer Birmingham product and after a while undertook to make its own steel at Alabama City, then a suburb of Gadsden, Ala. It built a plant there, which was unsuitably placed with reference to the supply of raw material and to the point of consumption. The company absorbed, by successive mergers, various other properties, which were heavily mortgaged, widely separated, and had too many interplant freights for the enterprise to be remunerative; it failed in 1907. In 1909, the company was reorganized and the rod and wire mill was removed from Ensley to Gadsden and largely improved, but sufficient capital was not provided to balance the plant or to furnish it with an adequate supply of raw materials; besides, it was still handicapped by the scattered condition of its properties. It failed again in 1912, after which a concern representing the bond-holders formed a new company, known as the Gulf States Steel Co. This company acquired the steel works and such other property as was considered desirable, relinquished much of the scattered and mortgaged holdings, and started afresh with modest capitalization. It was free from bonded debt, the holders having accepted stock for their bonds and had assessed themselves for fresh money with which to furnish an adequate ore supply at Shannon.

This mine represented a new departure in the Birmingham district. It involved a slope at a pitch of 50°, double-tracked, intersecting the ore at a linear depth of 2480 ft. and a vertical depth of 1905 ft. This was driven under much difficulty, as some mining engineers thought that the influx of water at very great hydraulic pressure would menace the mining operations. This danger, however, proved to be non-existent. On the contrary the mine was very dry, but the moisture of the air, attacking the shales, decrepitated both roof and sides to such an extent that it was necessary when the slope was nearly finished to begin at the top and widen and raise the section so that the slope could be lined with concrete—not to keep moisture in the strata, but to keep it out. This was successfully accomplished and 150,000,000 tons of nearly self-fluxing ore is now rendered available. That company has confined itself to the production of wire and its various products and to merchant bars. It added by-product ovens in accordance with modern practices, and is solidly established in business, pays a reasonable dividend and is operating free from debt.

After the withdrawal of the Alabama Steel & Wire Co., the Tennessee Coal, Iron & Railroad Co. was practically without a customer. Finding it impossible to pay the freight to northern markets and successfully compete there in the sale of billets, it completed its rail mill and developed at the outset a successful quality of rails—to the satisfaction of the various companies running into the district.

In 1907, the panic found that the control of the company was represented by large amounts of its stock pledged as collateral by various parties, in the hands of the Trust Company of America, which also held control of the stock of the Central Railroad of Georgia. Because of the condition of the financial interests of the country at the height of the panic, a conference was held in New York and arrangements were made for the sale of the railroad stock to the Illinois Central R. R., and of the control of the Tennessee Coal, Iron & Railroad Co., to the United States Steel Corpn.; the funds thus obtained were sufficient to stop the run upon the trust company and the panic was stopped. This transaction, so far as it related to the control of the Tennessee Coal, Iron & Railroad Co., was later attacked by the United States Government as tending to establish a monopoly, and a suit for dissolution of the company ensued. Decided unanimously in favor of the company by four Federal judges, the decision was appealed by the Government and for several years, while the litigation continued, it was impossible for any new developments to be made. After the right of the United States Steel Corpn. to own the property was finally settled, capital for successive developments was liberally supplied.

The works constructed in 1898 to 1900 were largely dismantled and rebuilt on a larger scale. The pig-and-scrap method was replaced by the duplex process, by which the metalloids are largely removed in a few minutes in a bessemer converter and the remainder eliminated in the open hearth in one-half the time otherwise required, thus enabling a very large tonnage production. The company has gone, step by step, in the development of the works rehabilitating the bessemer rolling mill, for the production of plates and bars, and more recently constructing mills at Fairfield, for the production of structural steel, plates and reinforcing bars, over 200 ft. in length. The byproduct ovens constructed in 1898, by the Semet-Solvay Co. have been superseded by extensive plants of Koppers' ovens. The various mining camps have been made model villages, with houses, commissaries, medical and sanitary arrangements fully in keeping with the best practices anywhere; the hospital at Fairfield, costing over one million dollars, is doubtless the largest and finest in the Southern States today.

When the United States entered the World War, in 1917, the great need of ships caused the United States Steel Corpn. to construct a new shipyard at Mobile. Of the steamers constructed at Mobile, many are now in regular service all around the world; some of them constructed

entirely of Alabama material and carrying cargoes of Birmingham rails, sulfate of ammonia or other products of the Tennessee Coal, Iron & Railroad Co., go frequently to Japan or China; while others, going to Brazil with similar products bring back cargoes of manganese ore from the United States Steel Corpn.'s property there to be manufactured into ferromanganese by the Tennessee company.

After the termination of the war, when it became apparent that there was a surplus of vessels, the shipbuilding yard was dismantled and much of the plant removed to Fairfield, another suburb of Birmingham, where it is now in active operation producing steel cars for the company's own use and for the railroads running into the district.

The company has also, more recently, undertaken the construction of an overhead railway to bring its own materials from its mines, only 6 miles distant, to the blast furnaces, either now existing or those projected in the not distant future, thus eliminating payment of railroad freight. At the point where this railroad terminates at Fairfield, the company is constructing an additional open-hearth plant of stationary furnaces, where it will consume its own production of scrap. At the same point, it is also building a plant for the production of sheets, which have not been produced anywhere south of the Mason and Dixon line.

In the immediate neighborhood is also located the extensive rod and wire mill plant of the American Steel & Wire Co., supplied with billets from the Ensley mill.

The establishment on a large scale of these operations has in every way justified the early dreams of those who hazarded their time, their money, and their reputation in efforts which, where they failed, failed only because of the inadequate scale on which they were attempted.

The failures referred to, including the establishment of a blast-furnace and open-hearth plant at Fort Payne with a totally inadequate supply of raw materials, are all accounted for either in that way or by lack of capital, involving experimentation on a scale so small as to preclude any economic success. Every well-balanced and adequately capitalized scheme undertaken has been successful and has enabled a supply of billets to be furnished to other concerns, such as the Atlanta Steel Co., maker of hoops and bands, which later changed its name to the Atlantic Steel Co., adding open-hearth furnaces and becoming a buyer of basic pig iron instead of billets and now producing, in addition to hoops and bands, bars and wire products. The Connors Steel Co. similarly has developed a successful establishment, producing hoops and bands and cotton ties from purchased billets; and the way is now open for many smaller and subsidiary concerns to come and locate in the district, deriving their supply of materials from existing sources.

Brief History of Metallurgical Practice in Cannon-making with Particular Reference to the Cast-iron Gun

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In this paper, as in so many discussions of an historical nature, there is little chance for original material and much has had to be rewritten from older papers, documents, accounts, reports, and the like, some of which are of doubtful authorship or contain conflicting statistics. Fully aware of these pitfalls, the authors have tried to quote the origin where possible, and also to seek further confirmation when the statement warranted it, but they cannot assume responsibility for certain facts and dates. The Encyclopedia Britannica was frequently consulted.

The authors wish to acknowledge assistance from Mackintosh-Hemphill Co. (formerly the Fort Pitt Works) and also from officials of the Watertown Arsenal who loaned valuable books and gave much necessary information. They are particularly indebted to Colonel Dickson of that institution. The data on modern guns were furnished by Mr. F. Brauer of the Watertown Arsenal; Mr. H. S. Chaffee assisted by obtaining records and data of work carried on by the Builders' Iron Foundry of Providence, R. I.

Three Epochs in History of Cannon

Among the great industries of New England, the manufacture of iron was the first to receive attention. Iron ore in considerable quantities was known to exist within the territory of the Massachusetts Bay Colony; and as early as 1629 some steps appear to have been taken toward the manufacture of iron by the Court of Assistants in London, under whose patronage the colony was founded. During the next ten years, deposits of bog ore were found in numerous ponds in the Plymouth Colony; and, in 1652, iron manufacture was begun at Raynham. The "Old Colony" was known as the main seat of this industry in New England, out of which grew a concern which was later to become one of the principal

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manufacturers of cannon for the United States Government, The South Boston Iron Company.[1]

It is possible to trace a few of the steps whereby New England's part in the ordnance manufacture came about, and to show what part this industry has played in history. It is not the purpose of this paper to delve into a detailed history of gun manufacture. A little review of the progress of guns through the several ages is, however, interesting, and perhaps will serve to connect, in a way, primitive methods of destruction with medieval and modern industry.

Ever since organized warfare played any part in history, we learn of mechanical appliances for throwing projectiles, and "engines invented by cunning men to shoot arrows and great stones" are mentioned in the Old Testament. However, the history of the gun or cannon, as we think of it today, is properly divided into three epochs.

The first epoch was from 1313 to 1520, when a material resembling gunpowder was used for propelling the shot, which was nothing but a stone. Although the manufacture of bronze was well advanced at this time, most of the large-sized guns were made of wrought iron, as it was a cheaper material. The second epoch, from 1520 to 1854, in which the propelled material was made from cast iron and the cannon were of bronze or of cast iron, passed with very little actual progress. The third epoch, from 1854 to the present time, is marked by tremendous progress. The round cast-iron ball has given way to elongated projectiles of steel, and the era of rifled guns practically dates from the beginning of this epoch.

The actual date and place of the making of the first cannon is a subject of much controversy and research. However, "the earliest known representation of a gun in England is contained in an illuminated manuscript. *De Officiis Regum* at Christ Church, Oxford, of the time of Edward II (1326). This clearly shows a knight in armor fixing a short primitive weapon shaped something like a vase and loaded with an incendiary arrow. This type of gun was a muzzle loader with a vent channel at the breech end. . . . These fire arrows were evidently very small, as only 2 lb. of gunpowder was provided for firing 48 arrows, or about 7⁄10 oz. for each charge."[2]

Two guns left by the English after the siege of Mont St. Michel in Normandy, in 1423, were made of wrought iron and the larger had a bore of 19-in. diameter. Bronze guns made of two pieces screwed together and weighing about 18½ tons were known to be cast at Constantinople in 1468. The front portion of these guns had a caliber of 25 in. and was made for stone shot weighing about 675 lb. These were used later against Sir John Duckworth's squadron when the Dardanelles were

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[1] The present Hunt-Spiller Mfg. Corpn. of South Boston.

[2] Ordnance, History and Construction. *Encyclopedia Britannica.*

forced; in this engagement six men-of-war were damaged and about one hundred twenty-six men were killed or wounded.

During the sixteenth century, with the introduction of iron projectiles, which enabled the use of smaller caliber, bronze guns were greatly favored. They were first cast in England in 1521 and iron cannon were first cast there about 1540, foundrymen from other countries going to England to teach the art. Dr. Richard Moldenke says[3] that a certain Thomas Johnson is mentioned as having cast forty-two 3-ton "great pieces of ordnance for the Earl of Cumberland, in 1595" . . . and at the time of Queen Elizabeth, England actually exported guns to the Continent. The bronze guns at that time, although smaller, were very long; particular mention is made of one at Utrecht in 1544, which was presented by Charles V to Henry VIII; it was 24½ ft. over all in length, and the caliber was only 4.75 inches.

Up to about the first of the eighteenth century, guns were cast hollow, and there appears to have been no attempt at standardization or classification; but about 1739, when the boring of guns from the solid was introduced by Moritz of Geneva, uniformity of caliber naturally followed. During the eighteenth century, however, little change was made in principles of construction. Guns were made smaller and were strengthened, and much progress was made in standardization and methods of manufacture of gunpowder. In the earlier periods, the explosive was often mixed on the fields; it burned slowly, and was never dependable.

During the first part of the nineteenth century, there was great progress in metallurgical science, but cast iron was the only metal considered suitable for large guns, while bronze was used largely for field guns. Steel guns were attempted but, as there was no way of forging large quantities of steel, the metal had to be welded in order to obtain sufficient material for one gun. The art of welding had not been learned, hence steel guns were apt to fly to pieces suddenly and were considered too treacherous to use. We learn from some of the investigations of old guns, especially in connection with these earlier steel models, that their failure was probably due to lack of knowledge in gun designing rather than to poor material.

However, a certain Peter Townsend of Noble, Townsend & Co.[4] is said to have produced in 1776 the first steel made in the province of New York, at first from pig and afterward from iron in the German manner. His son, the second Peter Townsend, was supposed to have made in 1810 the first blister steel produced in the state of New York. The latter did much to improve the manufacturing of his day and made early use of anthracite in the blast furnace.

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[3] R. Moldenke: "Principles of Iron Founding," 6, 1st Ed. McGraw-Hill Book Co., New York, 1917.

[4] E. C. Kreutzberg: Orange County Ironmaking. *Iron Tr. Rev.* (1924) 75, 159.

Early American Foundries

The Sterling Iron Works in Orange County, New York, was prominently connected with iron manufacture during and immediately following the Revolutionary War. The anchors for the first United States ships of war were made there, including those of the U. S. Frigate *Constitution.* Perhaps its greatest achievement was the great chain which was stretched across the Hudson River to prevent British ships from getting up to Albany and thence within easy communication with Canada.

Another plant of some importance was the Orange foundry at Arden, operated by Cunningham Bros. During the War of 1812, it produced cannon balls for the American forces and the Cunninghams were permitted to keep twelve men exempt from military service.

Cyrus Alger and the South Boston Iron Works

An important part in the vast metallurgical progress of the nineteenth century was played by Cyrus Alger, who was born at Bridgewater, Mass., in 1781 and died at Boston in 1856. He followed the trade of his father, who was a foundryman. In 1809, he specialized in ordnance work and founded Alger's Foundry in 1810, which was incorporated under the laws of Massachusetts in 1827.

His business at first was that of a general jobbing foundry, but he soon began to devise valuable inventions applicable to his trade, among which was an improved method of casting chilled iron rolls, by which the part subject to wear was of increased hardness. This was patented in 1811. He discovered a way of purifying cast iron, which gave it nearly threefold the strength of ordinary iron castings; this discovery proved to be of immense value to the manufacturers of cannon and heavy artillery. The cannon he made were put to extreme test and rarely failed. During the War of 1812 he cast large quantities of canon balls for the government.

Mr. Alger introduced the use of anthracite for melting iron in the vicinity of Boston, and adapted his furnace to its use. (He also devised the cylinder stove for the home.) He made a change in the reverberatory furnace for melting iron; by reversing the incline of he hearth he caused the molten metal to flow toward the flame where the heat is most intense.

The new firm incorporated in 1827 as the South Boston Iron Works began the manufacture of iron ordnance in 1828. Alger's method of purifying cast iron gave to the company great advantage in making iron guns, especially those of large caliber. This process consisted primarily of melting the original metal in a reverberatory furnace, known as an "air furnace," allowing the metal to remain in fusion for an extended period of time, or casting and remelting until such time as the refining

action gave to the metal the desired physical properties which were measured to a great extent by the increased density obtained.

In 1834, Alger made the first rifled cast-iron gun in the United States and during the next year commenced the manufacture of the first malleable iron guns. He later supplied many of these to the government. One invention followed another, among them the covering of a fuse hole on the inside of the shell with a wafer of lead which had to be taken out before the shell was fired, in order that the surface of the fuse might be

FIG. 1.—ALGER'S IRON FOUNDRY, FROM SOUTH BOSTON BRIDGE.

exposed, so that it could ignite when it was discharged from the gun. He manufactured the first bronze guns for the United States Navy heavy artillery and also for the state of Massachusetts.

In 1842, the Columbiad, then by far the largest gun cast, was turned over to the government by the South Boston Iron Works and a report to the Ordnance Board of the United States War Department said that the cannon furnished by this company afforded the most favorable results, and that the quality of the metal was unsurpassed. It was of 12-in. caliber and had a range of more than two miles.

Francis Alger succeeded his father and added to the importance of the company. The younger man was scientifically inclined. He wrote a valuable book on mineralogy and had the finest collection of minerals in the country, brought from all parts of the world. He was elected a member of the American Academy of Arts and Sciences and received an honorary degree from Harvard University. He was also a member of

the Boston Society of Natural History and for several years its curator of minerals. Francis Alger was often called to Washington in the interest of his many inventions and of his company, and died there on Nov. 27, 1863, while engaged in testing shells.

Cyrus Alger made many inventions and improvements in metallurgical science which were valuable to the United States Government and were destined to become the basis of the great advance in metallurgy which continued throughout the latter part of the century. Admiral

Fig. 2.—Casting a great cannon at the South Boston Iron Works, 1884.

Dahlgren once said of Mr. Alger, "He possessed that rare quality, sagacity, which constitutes in truth the highest attribute of the intellectual man, and enabled him to arrive at results which others sought by disciplined study, and often in vain." His process whereby irons of different analyses were put into the furnace charge and treated in the furnace, the resulting iron being cast in pigs and known as remelt iron, is familiar to all foundrymen of today.

In a report to the Ordnance Department on Apr. 2, 1844, Major Wade, of the United States Army, shows some of Mr. Alger's work in making tests on heating the melted iron for different periods of time, which were carried out at the Alger plant (South Boston Iron Works). Some of the results obtained were as follows:

	Strength, Pounds
First casting made as soon as pig was melted	6506
Second casting, iron in fusion 1 hr	7316
Third casting, iron in fusion 2 hr	8256
Fourth casting, iron in fusion 3 hr	8378

This report shows a gradual and positive increase of strength as the iron is continued in fusion for longer periods of time. The reports also conclude that a high temperature makes for soundness and greater strength, and goes on to say that although the transverse strength is that most generally measured, when the quality of different metals is compared, it is believed that a more accurate measure may be found in the tensile strength. Some of these figures are interesting in this connection.

	Density	Tenacity, Pounds
Guns cast prior to 1841	7.148	23,636
Guns cast in 1851	7.289	37,774
Samples from 10-in. Columbiad, 1851	7.304	45,970

The first of the large cannon[5] of 10, 11, and 12-in. caliber, for the United States Government, were cast by order of the government at the South Boston Iron Works under direction of Mr. Alger, the latter selecting the iron and using his own process. One of these guns, 11-in. caliber, carrying a solid shot of 170 lb. or a shell of 135 lb., was first fired 655 times with the former projectile, and 1306 times with the latter—an enormous endurance of 1959 rounds before it failed; far exceeding any other record of the Ordnance Department from this or any other country.

This process thenceforth was used a great deal for gun castings, and hence the metallurgical term "gun-iron" was created.

Foundries and Processes, 1840–50

The foundries casting ordnance between 1840 and 1850, in addition to the South Boston Iron Works, were the Fort Pitt Foundry at Pittsburgh, Pa. and the West Point Foundry at Cold Spring, N. Y. These foundries were using charcoal iron for gun castings which was obtained from the Greenwood Furnace near Cold Spring, N. Y., Franklin Smelting Furnace, New Jersey, the Ammenia Furnace and the Richmond Furnace, Richmond, Mass.

The method of casting the guns solid and boring out the interior was followed, but the exterior usually became chilled during the cooling process by sudden contact with the mold and was converted into a solid crust before the interior had even dropped to the melting temperature. The result was that the gun frequently consisted of strata of different densities, and although great care had been exercised by the founder it was not unusual to find a spongy portion consisting of crystals so loose that dark cavities could be seen with the naked eye. A sharp-pointed steel chisel could be easily driven into the spongy portion. It was not until Lieutenant Rodman devised a most remarkable process that extreme endurance service was obtained with guns manufactured from cast iron.

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[5] Guns of 8-, 10-, 15-, 20-in. diameter are technically known by the Army as Columbiads.

Rodman's Process

Thomas Jefferson Rodman was born at Salem, Ind., July 30, 1818. He was a West Point graduate and served in the Mexican War, but soon showed such skill in devising guns and ammunition that he was detailed to that work exclusively.

In 1849 he invented a process of casting hollow cannon by means of a core around a tube, or what might be called a core arbor; water was run in through a pipe in the inside of the tube to about five or six inches from the bottom, the tube having a closed end so that no water could leak out. The water circulated during the casting to a side outlet near the inlet, a sufficient supply being sent through the tube to keep it cool. Hence with the inner portions of the casting cooling and solidifying first, they were compressed and supported by the contraction of the exterior when it cooled. The casting was further secured from irregular or excessiv s trains by building a fire around the flask to keep it hot so that as uniform cooling as possible would take place. About 24 hr. after casting, the arbor was removed and a pipe was put in the bore of the casting that was formed by the core and a stream of water was passed through it until the casting was cold.

Most of Rodman's work was carried out at the arsenals at Pittsburgh, Watertown, Mass. and Rock Island, Ill. At the last named, he was in command from 1865 until his death on June 7, 1871. He rose to the rank of Brigadier General by brevet.

The first guns made by his process were cast at the Fort Pitt Foundry, Pittsburgh, on Aug. 4, 1849. They were two 8-in. Columbiads. Some of the experimentation connected with the manufacture of these guns and also the manner in which they were tested are described in detail by Rodman in his reports. The two molds were placed side by side in a pit and the iron charged in two air furnaces, each containing 14,000 lb. of the same kind of iron. After melting, the liquid iron remained in the furnaces one hour exposed to a high heat and was then discharged by separate streams into a common reservoir; from the reservoir it issued into a single stream, which after proceeding a few feet separated into two branches, each leading to a separate mold. Both molds were filled at the same time; one was cast solid, and one was cast hollow and cooled by the Rodman process. The testing of the guns commenced Sept. 7. The one cast solid burst at the 85th fire; the one cast hollow and cooled by the Rodman process burst at the 251st fire. The density of the iron used was 7.223; the tenacity, 27,488 lb.

Again, two 8-in. guns were cast on July 30, 1851. The iron was made at Greenwood Furnace, New York, and was 36 per cent. of No. 1, 25 per cent of No. 2, and 39 per cent. of No. 3. The iron (28,000 lb.) was melted in two furnaces; 12,500 lb. in one and 15,500 lb. in the other, nearly three-

fourths being of second fusion, one-fourth third fusion, and the remainder fourth fusion. After melting, the liquid iron remained in the furnace 2½ hr. exposed to a high heat and was then discharged by separate streams into a common reservoir; at the same time it was withdrawn from the reservoir in a single stream, which, after proceeding a few feet, separated into branches leading to separate molds and filled both molds at the same time. One of the castings was made solid and cooled in the usual manner. The other was cast hollow and cooled by the Rodman process. A fire was kindled in the bottom of the pit directly after casting and was continued 60 hr.; the pit was covered and the iron flask

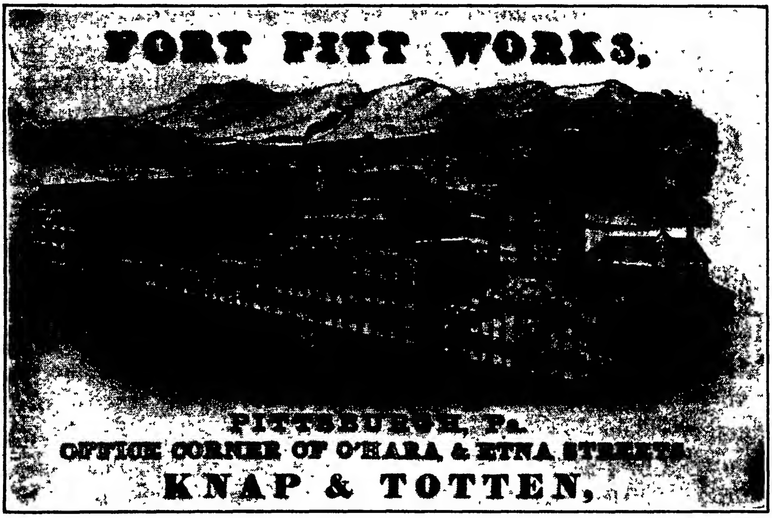

Fig. 3.—Fort Pitt Works, founded 1803 as the Pittsburgh Foundry. It cast the first guns by the Rodman process in 1849.

containing the mold was kept at as high a temperature as it would safely bear.

The testing of these guns commenced Aug. 28, and continued until Oct. 22. The one cast solid burst at the 73d fire and the one cast hollow burst in the 1500th fire. The density of the iron used was 7.287; the tenacity, 37,811 lb.

Again two 10-in. Columbiads were cast on Aug. 21, 1851. Greenwood iron of the same qualities as melted for the 8-in. guns was used. About one-ninth consisted of first fusion; five-ninths of second fusion; and one-third of third fusion. It was melted in three air furnaces containing 12,000, 15,000, and 19,000 lb.—in all, 46,000 lb. The liquid iron remained in fusion 2¼ hr. and was discharged from all the furnaces at the same time into a common reservoir, from which it issued in a single stream. After proceeding a few feet, it separated into two branches, leading to separate molds, both filling at the same time. Both molds were placed in the same

pit. One of the guns was cast solid and the other was cast hollow and cooled by the Rodman process as described above. All the pit outside of the molds was filled with molding sand and rammed because the iron flasks were not large enough to admit the usual amount of sand in the walls of the mold.

It was feared that the heat of the great mass of iron within would penetrate the thin mold and let the iron run out; consequently the exterior of the mold of the 10-in. hollow gun, instead of being exposed to the heated air while cooling, was surrounded by green sand, which caused a more rapid cooling of the exterior surface of the casting. Water was passed through the core arbor for 94 hr. at the rate of about 30 gal. per min. At the end of the period, an attempt to withdraw the core arbor proved unsuccessful; the contraction of the iron around it held it so firmly that the upper part broke off, leaving the remainder imbedded in the casting. The stream of water was then diminished to 15 gal. per min., which continued to circulate through the arbor for 48 hr.

The testing of these guns was commenced Oct. 7 and ended Oct. 18, 1851. The one cast solid stood 20 fires; the one cast hollow and cooled by the Rodman process stood 249 fires. The density of the iron used was 7.292; the tenacity, 37,817 lb.

"It will be seen[6] that the endurance of the guns cast hollow surpasses those cast solid in every case where both were cast in pairs at the same time and from the same material, the difference in one case being more than twenty to one, and the aggregate of all, more than eleven to one. This great difference occurring in every instance where guns were cast and tried in pairs could not, it is believed, have been caused by any accidental circumstances, for the methods pursued to insure an exact equality of material in both guns of each pair and for preserving an exact uniformity in the proof of each, seem to forbid the supposition that any unknown inequalities could have existed, either in the casting or the proving of the guns. The great difference of endurance must therefore be ascribed to the different methods by which the castings were cooled, and to those above.

"It will be perceived, also, that in the several pairs cast solid and hollow, the actual strength of the iron in each gun of the pair as measured by the testing machine remains the same, while the strength of the guns in the same pair, as measured by the fires endured, differs greatly. From this it appears that the difference in the methods of cooling the casting, while greatly augmenting the strength of the gun in one case does not impair or affect the strength of the iron. For these and other apparently discordant or incongruous results, we must seek an explanation in the laws which govern the contraction of iron when cooling. It is known also

[6] "Reports of Experiments on the Strength and Other Properties of Metals for Cannon." Govt. Report, 1856.

that the contraction under equal reductions of temperature is different in iron of different qualities; soft gray iron, that which contains a high proportion of carbon, contracting least; and that which founders term high, which is light and close grained and contains the least percentage of carbon, contracts the most. Other circumstances being equal, the contraction of the same iron is greater or less according to the greater or less rapidity with which it is cooled. That which is cooled most rapidly contracts most. Every experienced founder is aware of this and endeavors so to proportion his patterns that all the parts of the same casting may cool equally.

"A convenient method for determining the condition of the iron while in fusion, and whether it has arrived at the proper condition for casting or should be longer in fusion, is found in dipping from the melted pool of iron and casting into small bars 10 in. long, 2 in. square at the top, down to 3/4 in. at the bottom in a step form in four sections. They are cast open in green sand and allowed to remain in the sand 10 min., then taken out and cooled carefully with water, then broken at the different places and the condition of the iron judged by the several fractures. These fractures will exhibit various aspects from white at the small end to a mottled in the middle, and to a dark gray at the large end; and a practiced eye will soon be able to mark the process of the changing quality of the iron and to determine the proper time for casting the gun."

The Dahlgren Gun

Alger made a 12-in. Columbiad in 1842, and subsequently the original experiments resulting in the famous Dahlgren "shell guns." Doctor Moldenke again tells us[7] "that between the years of 1862 and 1877 alone, no less than 272 Rodman guns, of which 103 were of 15-in. caliber and weighed about 50,000 lb. apiece, were produced at this establishment."

The Dahlgren gun was a gray-iron gun and was designed about 1840. It differed from the Rodman gun in that it was cast solid, cooled from the outside, and bored out. Both were smooth-bore guns and each was named from the officer who designed it—Rodman of the Army and Dahlgren of the Navy. W. P. Hunt tells us[8] that "the 11-in. Dahlgren gun carried by the *Monitor* in her fight with the *Merrimac* and the guns of the same type which sunk the *Alabama* were made at the South Boston Works."

Earliest 15-inch Guns

In 1860, Mr. Rodman constructed his huge 15-in. cannon and his mammoth powder and cake powder, the last named being quickly adopted throughout the world. These devices proved to be of great

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[7] R. Moldenke: *Op. cit.*, 5.

[8] *Iron Molders Jnl.* (March, 1906).

value to the government in the Civil War, and were widely used in both the Army and the Navy.

During the latter half of 1859, Rodman, who was a captain at that time, carried out at the Watertown Arsenal exhaustive experiments to determine the proper quality of iron for casting into a 15-in. gun. As a result of these experiments it was determined to make the gun from remelt Bloomfield iron, and it was cast at the Fort Pitt Foundry (38 tons of iron charged) on Dec. 23, 1859. The casting was made entirely by the Rodman process and it was the first 15-in. gun made. Water circulated through the core arbor at the rate of about 40 gal. per min., entering at 36° F. and leaving at 60° F. After 24 hr., the core arbor was removed and water circulated through the cavity thus left at the rate of 43 gal. per min. The time required for cooling was 168 hr. Specimens taken from the chase of the gun gave a density of 7.216 and a tenacity of 34,187 lb.

When the war broke out in 1861, the South Boston Iron Works was called upon to make extensive additions to its plant and to undertake the construction of cannon of much larger bore than had then been made. A new foundry was built and equipped with three air furnaces, each of 45 tons capacity, and a large number of 15-in. guns were made, each weighing about 50,000 lb. Previous to the war, the ordnance work of the government was handled by four foundries—the South Boston Iron Works, the West Point Foundry, the Fort Pitt Foundry, and the Tredegar Foundry at Richmond, Va. Other foundries were pressed into service for the war only, and for the construction of guns of small caliber almost exclusively. During the war, the West Point Foundry was devoted to the manufacture of the Parrott gun. The government then was largely dependent on the South Boston Iron Works and the Fort Pitt Works for its heavy ordnance, and the South Boston Iron Works also made large quantities of projectiles, rifle guns, and the Schenkl projectile.

Greenwood Furnace and the Parrott Gun

The Parrott gun was a gun of the smaller type invented by Robert P. Parrott, a former army officer. He was born in 1804 in New Hampshire and graduated from West Point in 1824, about nineteen years before Lieutenant Rodman. He was made a captain in 1836 after having fought in the war against the Creek Indians. He was first stationed at the West Point Foundry but in 1839 he and his brother Peter purchased the Greenwood Furnace and its ore and woodlands from a Mr. Kemble. They experimented there with charcoal pig iron and hooped guns.

The well-known Greenwood charcoal furnace[9] "originally was about 36 ft. high with tuyere arches on each side but none at the back . . .

[9] E. C. Kreutzberg: *Loc. cit.*, 285.

In February, 1839, the bridgehouse and all of the woodwork about the furnace, excepting the waterwheel (supplying power for the blast), were destroyed by fire. In rebuilding, the height of the stack was raised to 42 ft. and new blowing machinery was installed. The output thus was increased to about 30 tons of iron a week . . .

"An interesting feature of the operation of the Greenwood Furnace is that it was customary to smelt without any limestone. This was because the native ore to a large extent was self-fluxing. The O'Neil mine yielded ore which could be used without any limestone whatever. The Greenwocd Furnace was operated on this ore for a period of two years without any limestone . . .

"One of the interesting achievements there was the casting of guns for the navy in 1855–56 direct from the blast furnace."

R. D. A. Parrott, of Flushing, N. Y., in a memoir published a few years ago, describes the operation of the furnace as follows:[10] "The ores were not hauled directly to the furnace, but to a kiln half a mile above it, in which they were roasted to drive off the sulphur. After this they were put through a stamping mill which reduced the size of lumps to that of a pigeon's egg . . . An important branch in the business was the cutting annually of 10,000 cords of wood and turning it into charcoal."

At the outbreak of the Civil War, Robert Parrott presented his first hooped gun to the government. This proved to be a very satisfactory piece, and large orders were immediately placed, which created a big demand for charcoal iron. The Parrott guns began operating at Fort Sumter and were continually supplied to the government throughout the war. The Parrott gun was described by Mr. Parrott[11] as "a hooped gun of the simplest kind, composed of one piece of cast iron and one of wrought iron. It had no taper, no screw, no successive layers of hoops. It was, however, no hasty expedient, but was devised upon the results of years of experience and practical trials, and had a definite and consistent plan." In fact, it was a gray-iron rifle with a wrought-iron band to reinforce the breech.

Both the Army and Navy Departments insisted on charcoal iron made by the cold-blast method, and a Lieutenant Walker of the Navy was stationed at Greenwood to see that this method was the one used. As the men at the furnace were used to the hot blast and desired to run the furnaces accordingly, a valve was constructed whereby the air could be readily shifted through the heater or not as desired. A foreman later related that it was customary to run on hot blasts until "Lieutenant Walker was seen coming around a bend in the road, whereupon the valve was closed and the furnace put on cold blast. The hot blast was about 120° F., the maximum then obtainable."

[10] E. C. Kreutzberg: *Loc. cit.*, 287.
[11] *Laclede Christy Bull.* (June, 1921).

Improvements in the Bronze Cannon

During the period of depression through which ordnance concerns had to pass shortly after the war, the Fort Pitt Foundry closed its doors, and since the West Point Foundry was adapted for making guns of smaller caliber only, the government became more and more dependent on the South Boston Iron Co. for heavy ordnance. The master mechanic at that plant came forward about this time with a very important improvement in the manufacture of bronze cannon and a patent was granted to him in 1869 for his invention. This improvement consisted of a method whereby the interior metal of the cannon was made more dense, thus increasing its strength and wear. After the piece had been bored and rifled, a mandrel of slightly greater diameter than the bore was forced in by hydraulic pressure, following which others of increasing size were forced into it. This, of course, renders the metal near the bore of greater density and consequently of more resistance to abrasion in firing. Bronze cannon made by the usual method wear very rapidly, especially if rifled. By Dean's method, however, they become as durable as steel guns.

Post-war Work at South Boston Iron Works

We learn again from Mr. Hunt's article in the *Iron Molders' Journal* that immediately after the Civil War large orders for guns and ordnance were received by the South Boston Iron Works for South American republics. About 1867, war was declared between Spain and Chile and Mr. Hunt, who was an official of the South Boston company, says, "We shipped to Chile three 1000-ton cargoes within the period of six months; also large shipments to Peru later on, and to Argentine Republic, ten 25-ton Rodman guns. Our contract with the Argentine Republic was 'free on board at Boston' and the guns were promptly shipped to Buenos Aires. When the captain returned to Boston, we learned that the officials there had no means of taking the 25-ton guns from the vessel, and to avoid damage they concluded it would be economical to pay the captain $60,000 for his vessel and send him home."

In 1875, the South Boston Iron Works cast a 12-in. steel-lined rifled gun under the patent of Nathan Thompson of Brooklyn, N. Y. It weighed 80 tons when cast and 45 tons when finished and was breech-loading.

During 1877, a muzzle-loading cast-iron gun lined with wrought iron was made by this company and was the largest gun ever cast up to this time. It was rifled and weighed when finished 45 tons. The wrought-iron tube weighed 13,000 lb. and the gun itself 77,000 lb. It fired a 600-lb. shot.

Apparently the next contract given out for cast-iron guns was one for two guns of 10-in. caliber, and two of 12-in. caliber, to the South Boston Iron Works, in 1880. Owing to the extensive preparations necessary in the work of casting these guns, they were not completed until 1884. A detailed description of the casting appeared in *Foundry* (January, 1918). The article was written by Job Goostray, assistant to

FIG. 4.—CIRCULAR ISSUED BY SOUTH BOSTON IRON CO.

James Wood, who had charge of the work. Mr. Wood was foreman of the ordnance-casting department of the South Boston Iron Works.

The first gun was cast by the Rodman method and when finished was 25 ft. long and weighed 28 tons. It was taken to the Watertown Arsenal to be wound with wire, and was known as a 10-in. wire-wound rifle.

The second gun was to be a 12-in. breech-loading rifle to be cast breech up. This was also cast by the Rodman process and when finished weighed 54 tons and was 30 ft. long. A contract was made with a building mover to remove the gun from the pit and place it in the lathe for the sum of $550. It took the contractor five weeks to accomplish the work.

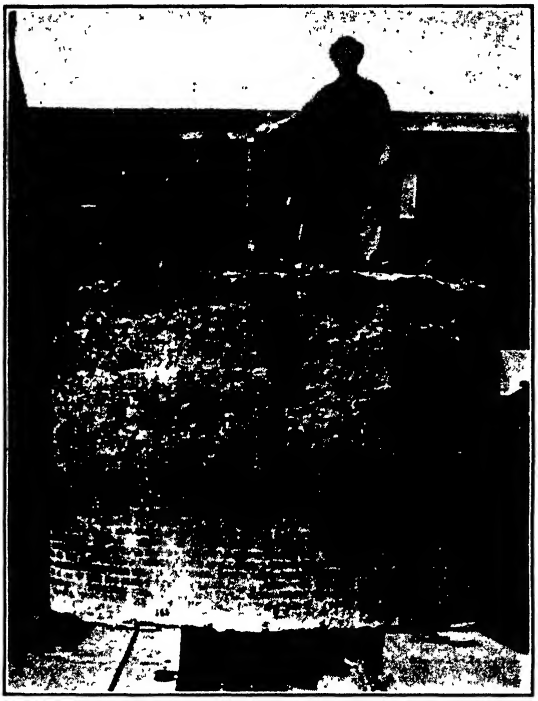

FIG. 5.—THE 120-TON GUN THAT FELL TO THE BOTTOM OF THE PIT WHEN THE FLASK FAILED AN HOUR AFTER CASTING.

The third gun was also a 12-in. breech-loading rifle and was to be cast breech down. It was the heaviest gun cast in the United States up to that time. This was not as successful as the two previous castings, for about an hour after being cast, the flask gave way, the iron going to the bottom of the pit. As there was approximately 120 tons of iron involved in the casting, there was quite a loss represented by the accident. The result is shown in Fig. 5. This caused some delay in carrying out the work and it was not until October, 1884, that work on the contract was resumed. The next gun attempted was one of the hoop and tube type. The casting weighed approximately 76 tons and was entirely successful.

Work was again begun during the following month on a 12-in. breech-loading rifle similar to the one that caused the trouble before. This was

cast successfully but was rejected by the government because of a small crack in the interior discovered during the machining process, which was apparently due to too rapid cooling. Likewise, another gun of this type,

FIG. 6.—EXTERIOR VIEW OF CASTING HOUSE, ALGER'S FOUNDRY.

cast in August, 1885, proved defective, because of the washing away of the coating of the core arbor, which allowed the iron to get into the interior.

FIG. 7.—MACHINING A 12-IN. BREECH-LOADING 54-TON RIFLE AT THE SOUTH BOSTON IRON WORKS, 1884.

During the early part of 1886, a successful casting of this model was made. The mold was filled in 33 min. and was allowed to cool very slowly for several days. After the South Boston Iron Co. had completed

this contract, work was started on 30 breech-loading mortar bodies. These averaged 18 ft. long, were of 34-in. diameter, and weighed over 20 tons each.

Large Guns at Fort Pitt Foundry

Frequent reference has been made to the large 15-in. guns, and it is interesting to note that this caliber is close to the upper limit even on the modern gun. The Fort Pitt Foundry, however, did cast at one time two 20-in. guns, one for the Army and one for the Navy. The former weighed 116,497 lb. and the latter 100,000 lb. Each cannon fired a 1000-lb. shot. Artillery as large as this did not prove practical, and these guns became much more interesting than useful. It is also interesting to note, in connection with the large diameters, that the Fort Pitt Foundry also made one hundred and fifty 18-in. mortars, which were more in line with the abilities of the foundries at that time but were never adopted by the government to any great extent.

Defense Program of United States, 1885

In May, 1885, there were available for seacoast defense the following smooth-bore Rodman guns: two 20-in.; three hundred eighteen 15-in.; nine hundred ninety-eight 10-in.; two hundred ten 8-in. In addition, there were two hundred ten 10-in. Rodman guns that had been converted to 8-in. rifles by the insertion of a steel liner. There were also available for the defense at this time thirty-eight 300-lb., eighty-one 200-lb., and one hundred seventy-three 100-lb. rifled Parrott guns. A report indicates that these Parrott guns were of doubtful strength.

By act of Congress, Mar. 3, 1885, the President of the United States was authorized to appoint a board of which the Secretary of War became a member and president. This board was called "Board on Fortifications or other Defenses." The purpose of this board was to examine and report the conditions as found to exist at the various forts, fortifications, or other defenses, and to determine the character and kind of equipment most urgently required and best adapted for each with reference to armament, etc. An extensive program was prepared by this board, taking in defenses of the whole United States, not only seaboard cities but also lake ports. This program recommended appropriations for the manufacture of 6-, 8-, 10-, 12-, 14-, and 16-in. guns and 10- and 12-in. mortars with the carriages, emplacements and accessories.

In connection with this system of coast defense, a contract for fifty 12-in. breech-loading rifle mortars, with a cast-iron body, and steel-hooped, weighing 14¼ tons, was placed with the Builders' Iron Foundry of Providence, R. I., and orders for the finishing and assembling 73 of these mortars were likewise placed with that company.

"These mortars[12] in appearance very closely resemble the steel breech-loading rifles made by the United States Navy Department, with the exception of their length, which in the rifles is about thirty times the diameter of the bore and in the mortars only ten times." The bodies were to be made of charcoal iron and cast breech downward. The outside diameter over the steel hoops, which were shrunk on the bodies in two rows, was 42½ in. A complete description of the casting and specifications for these mortars is given in the booklet published by the Builders' Iron Foundry.

The Builders' Iron Foundry had been prominent during the Civil War in ordnance manufacture and had since from time to time received important contracts for government work; this comparatively large contract for Rodman guns was practically the last order for cast-iron guns. There were, of course, many 8-, 10-, 12-, and 16-in. guns to be built in connection with the recommendations of this "defense board," and it was at this point that the ordnance engineers and experts began to realize the limitations of cast iron and consequently began to turn their attention to the manufacture of steel guns. This was because the casting of cast-iron guns was a matter of trial based upon previous experience and thus became more or less of a "rule of thumb" method, while in the case of steel it became a matter of an exact science in that the physical properties of the steel could be predetermined by calculation. However, in 1885, there was no plant in the United States capable of making forgings for guns of more than 6-in. caliber.

Some time previous—1883—a group of men known as the "Endicott Board" was appointed to investigate the gun and steel establishments in the United States and abroad. This board recommended that the United States Government maintain gun factories capable of turning out the largest caliber after the most approved patterns and that private firms be encouraged in making steel forgings and material for guns. Therefore, in 1886, $4,000,000 was appropriated for a steel-armor plant and $2,128,000 for guns. The Midvale Steel Co. and the Bethlehem Steel Works were given contracts for forgings and each undertook the manufacture of 100 guns of various calibers, these guns being practically all called "model of 1886."

Adoption of Alloy Steel for Guns

It is practically from this date that the alloy-steel gun came into existence in the United States as a means of defense for the coast ports. It was to take the place of the cast-iron Dahlgren and Rodman guns which heretofore had been the armament of the defenses.

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[12] "12-Inch Breech-Loading Rifled Mortars." Booklet published by Builders' Iron Foundry.

Capt. F. E. Hobbs, Ordnance Dept., U. S. Army, made some investigations of hollow steel forgings that were cooled from the interior during the process of manufacture. This was with a view of introducing internal stresses, which would be helpful in opposing interior pressure on the cylinder. He also investigated the process of shrinking hoops over cylinders or tubes for the purpose of accomplishing these same results. This experiment was carried out in 1892 on a tube whose wall thicknesses were practically that of a 3.2-in. field gun. A careful examination of the guns so manufactured indicated that the initial stresses were properly disposed, varying from compression at the bore to extension at the interior.

This forging was given a thorough physical test by cutting off rings and specimens. It developed physical characteristics that left no room to doubt that initial tension strains of as great intensity as are desirable could be produced in a hollow forging. Experiments also indicated that if these strains should be more than were required they could be reduced by annealing.

Modern High-power Guns

All modern high-power guns are made of steel and are composed of several parts united to form a whole with the parts so arranged as best to support the stresses upon them. Therefore the gun is called either a "built-up" gun or a "wire-wrapped" gun.

In order to obtain an initial compression of the tube or inner member of a built-up or wire-wrapped gun, an exterior pressure is exerted by placing over the tube a heated cylinder or hoop whose interior diameter is slightly less than the exterior diameter of the tube. When cooling, the hoop contracts and if the difference of diameters is properly regulated it will produce the required pressure and thus initial compression of the tube. The compressing and strengthening of the tube, however, will in some measure extend and weaken the hoop shrunk on the outside, but this extension or weakening when properly regulated can be supported without damage to the structure. In other words, the modern cannon is made of concentric cylinders shrunk one upon another, the object of this method of construction being twofold; first, the attainment throughout the steel of each cylinder of soundness and uniformity of metal, and second, the best results according to the theory of gun construction. The steel employed in the making of guns must be of the highest quality and the finest grade. It requires the most expert knowledge of steel manufacture.

The 16-in. 50-caliber gun is the largest and most powerful piece of ordnance in the United States at the present moment and with an eleva-

tion of about 54° and a powder charge of 850 lb., and a projectile weighing 2340 lb., will have a maximum range of about 31 miles. This is a wire-wound gun 70 ft. overall and weighing with breech mechanism and recoil band 385,847 lb. The velocity of rotation of the projectile as it leaves the muzzle, due to rifling, is 1620 revolutions per minute. The material used in the construction is alloy nickel steel having an elastic limit of 65,000 lb. per sq. in. The wire used is $\frac{1}{10}$ in. square, cold-rolled alloy steel. It is wound on the gun at a stress of 50,000 lb. per square inch.

Fig. 8.—Modern 16-in. 50-caliber rifled gun, firing at an elevation of 54° with a range of 31 miles.

In a gun of this length, due to the weight and elasticity of the metal, there is a droop, when the gun is in a horizontal position and supported in its cradle, of anywhere between 0.5 and 0.6 inch.

The magnitude of the construction of a gun of this size can more readily be understood by the size of the ingots and forgings which are approximately as follows:

	Ingot, Pounds	Forging, Pounds
A tube	194,112	48,528
B tube	275,992	68,998
C hoop	91,536	22,884
D hoop	315,532	78,883
E hoop	162,508	40,627
Jacket	123,328	30,832
Breech block	10,768	2,692

The accuracy life of some of the cannon now in the United States without requiring relining is as follows:

	Rounds		Rounds
75-mm. gun	10,000	6-in. seacoast guns	1,000
3-in. gun	5,000	8-in. seacoast guns	800
4.7-in. gun	5,000	10-in. seacoast guns	700
155-mm. gun	2,500	12-in. seacoast guns	600
155-mm. howitzer	7,000	14-in. seacoast guns	400
240-mm. howitzer	6,000	16-in. seacoast guns, 50-caliber	100
5-in. seacoast guns	1,000		

It is probable, however, that cannon can be fired to about 50 per cent. above these figures before relining.

German Long-range Cannon

This résumé on guns would not be complete without mentioning the greatest achievement of the twentieth century, the long-range gun developed by the Germans and used by them in shelling Paris in 1918. This cannon had the characteristics of abnormal range and used a projectile grooved to fit the rifling of the gun. It is probable that a 381-mm., 45-caliber naval gun was retubed to a diameter of 210 mm., which will make the length of this gun about 140 calibers.

While the powder used is yet unknown, it has been computed with a projectile would probably have about 5200 ft. per sec. velocity and would carry a projectile of 264 lb. a distance of 76 miles.

The elevation of the gun for this fire was probably about 54° and the projectile mounted to a maximum height of about 24 miles in traversing the trajectory of 90 miles between the gun located in the Forest of St. Gobain near Laon, and Paris. It would take about three minutes for the projectile to travel this distance.

The great range was obtained, no doubt, because the projectile traveled in lighter strata, which would offer less resistance to its flight, and because a comparatively small projectile was used with a large powder charge in the chamber made for heavier projectiles.

Conclusion

In warfare, as in peaceful ventures, one improvement follows another and perfection is seldom reached. The final improvement of today is a stepping stone to the new one of tomorrow. It is well; for such men as are willing to devote themselves to science and research must have fields sufficiently large to repay them for their study. The most difficult tasks become easy when progress is shown, however slight the progress may be. The authors hope that this paper has brought out the progress of the past, some of the facts and problems connected with it, and the possibilities, in this field alone, of scientific study in the future. It is not complete, but may serve as a connecting link between detailed reports of the past and scientific descriptions of the present.

DISCUSSION

A. G. Zimermann,* Washington, D. C.—I would just like to round out this excellent paper by showing that the art of gun-making follows cycles, somewhat like those occurring in every other line of endeavor. We have just heard how the gun formed of a single piece was succeeded by the built-up gun; the most modern way of making guns is to make them out of single pieces of steel, thus going back to the mono-block idea. Both Professor Bridgman, of Yale, and Mr. Albert Emery, of Stamford, Conn., advanced this idea and, I am convinced, developed it independently.

The first gun made in the United States by this process was in 1918 at the Naval Gun Factory, in Washington.[13] It consisted of simply a single piece of steel bored to the approximate dimensions and subjected to a very great internal pressure so that the metal began to flow, and the exterior, of course, expanded. The elastic limit of the material was thus raised and we were able to get the strength from a single piece of material that before had been considered impossible except by either wire winding or by building up one hoop after another.

The French used the same system, and had been building guns by this process some two years before we did. They considered the process a secret, however, and were surprised to find that we had been working on the same thing. There is a limit to which, with the pressures available, we can build guns of this kind. The largest made so far have been 6-in. but I understand 8-in. are contemplated. There are all indications that the gun of the future will be a compromise between this radially expanded single piece of metal and the assembled concentric hoops.

George A. Orrok,† New York, N. Y. (written discussion).—To those of us whose forefathers took part in the wresting of the Old Bay State from the wilderness, who raked the bog ore and ran their crude furnaces under the protection of "Brown Bess," the authors have not gone far enough. While the Lynn and Saugus sites were occupied as early as 1638 and small amounts of iron were made, the Plymouth County bog-ore deposits were known as early as 1650 and by 1685 at least three towns—Situate, Pembroke and Halifax—were casting pots and cannon balls. The Raynham forge, built by the Leonards, dates from 1652 and Bristol County had at least three other works in operation in 1685. Iron was made in Bridgewater first about 1690; in 1738 Hugh Orr, a Scotch gunsmith, escaping the English law against the migration of mechanics, put

* Lieutenant Commander, U. S. Naval Gun Factory.

† Consulting Mechanical Engineer.

[13] P. W. Bridgman: Experiment in One-piece Gun Construction. *Trans.* (1922) 67, 1145.

up the first trip hammer and made the American muskets. He also made scythes and shovels. His works later became the Bridgewater Iron Works, and there the elder Alger worked along with the Reeds, Careys, and Perkins. Cyrus Alger probably learned his trade at the Bridgewater Iron Works. I have been told that the Ames works in Easton secured their shovelmakers from Orr in Bridgewater. During the Civil War, the Bridgewater Iron Works covered 17 acres, employed over 1600 men, and made forgings, anchors, shafts, ship truss work and armor, castings, cannon and shells. Forgings for Ericson's "Monitor" and shafting of 40 tons weight were among the important work turned out. Stetson and Ferguson are the two names to be remembered during this period. Halifax and Carver furnished cannon balls for the Colonial forces in the Louisburg campaign in 1755, and nearly every town in the county made iron in small quantities during the Revolution.

My earliest recollection of Plymouth County is the little forge built at the side of every old farm house. Most of them, in my day, had been converted into shoe shops and the two-horse covered wagon bringing round the dozens of shoes for the farmer and his sons to sew or peg in their spare time was a common and regular sight. But the old forge and bellows remained in the corner and once in a while the nail anvil. In 1800, the two counties, Plymouth and Bristol, had eight slitting mills with a capacity of 7000 tons of nail rod per year. These rods were distributed to the farmers, just as the shoe materials were later, and the farmer and his sons made nails in their spare time. The invention and improvement of the nail-and-tack machine by Ezekiel and Jesse Reed (1810–20) drove out the hand forged nail; just as Keith's collection of the shoemakers into one building at Campello, in 1873, drove the last Yankee home industry into the factory system.

Among the other iron works in eastern Massachusetts employing considerable numbers of men were the Norway Iron Works, in South Boston, the Commercial Point Iron Co., the Wareham Iron Co., Tremont Iron Co., and Taunton Iron Works at Squabetty. Southeastern Massachusetts is dotted with slag piles.

Gun iron, on which most of these foundries made their reputation, is an extremely good material; 25,000 to 40,000 lb. tensile strength can easily be obtained when good materials are chosen and charcoal iron is not necessary for this good performance, as the same results have been obtained with coke or anthracite pig. The process is a refining one and if carried on for a sufficient length of time under proper conditions, the bath would come to nature producing wrought iron. The good qualities of gun iron induced John Van Vleck, formerly mechanical engineer of the New York Edison Co., to propose its use for his "Cannon" system of steam-piping, which he installed at the Duane Street station of that company in in 1893 to 1898. Wrought-iron pipe larger than 6 to 8 in. was very costly

and uncertain in the welds, so most power-plant engineers used riveted pipe when large diameters were required. This necessitated a gang of boilermakers in the stations at all times and the leakage was heavy. Mr. Van Vleck proposed the use of 200 lb. steam pressure for Duane Street at a time when 125 lb. was the standard and for piping 12-, 14-, and 18-in. gun-iron castings, using a ground joint and bolting the flanges together, metal to metal. Most of this material came from the Bridgewater Iron Works, the West Point Foundry, the Newburgh Foundry, and a foundry in Lebanon, Pa., and was of a very good quality, the transverse strength being very high. The bends were of copper, wound with a strip or wire, after 1898, these bends were replaced with steel-pipe bends, which were then obtainable. This steam piping, after 30 years of service, is still in use and is in excellent condition. Almost no money has been spent on the pipe for repairs and leaky joints have been rare.

F. Brauer, Watertown, Mass. (written discussion).—In this brief résumé of the history of gun construction in the United States, the period covered will be approximately the last century. An act of May 14, 1812, transferred all artillery construction from the engineers and the artillery over the Ordnance Department; this department, therefore, has been charged with the manufacture of artillery since the War of 1812.

The guns used during the War of 1812 were mostly cast iron, although some of the states secured a few bronze guns for the use of their state artillery. The first real attempt to establish a complete system of artillery was made in 1818, when the Secretary of War appointed a board of officers to make recommendations as to future construction. This report was submitted in 1820 and recommended that cast iron be used for all types of guns, but nothing definite was decided on, although there was considerable discussion in Congress and an act was passed to reduce the army.

In 1839, another Board of Officers was directed, by the Secretary of War, to prepare a plan for a uniform system of artillery. All the principal arsenals, foundries, armories, and shipyards in Europe were visited and valuable information obtained. The final report of the Board was made in 1841 and formed the first great advance toward the establishment of a uniform system of artillery.

About 1841, there appeared an interesting gun design by Prof. Daniel Treadwell. This design consisted of rings, or short hollow cylinders, of wrought iron joined together end to end by welding. Each ring was made of several thinner rings, placed one over the other and welded. Later, the method was changed; a ring of steel about one-third of the whole wall thickness was made and upon this a bar of wrought iron wound spirally and welded, as a ribbon would be wound upon a block. Machines were devised for making the rings, welding them together, and forming the

guns by means of various molds, dies, and sets connected with a powerful hydrostatic process. The object of this method was to so dispose the metal as to place the direction of the fiber in opposition to tangential rupture. Professor Treadwell's idea was to make a gun of equal strength in all directions and he demonstrated the proposition that the tendency to tangential rupture would be several times greater than the tendency to transverse rupture. Hence, he approached as nearly as possible with the means and information available, the ideal gun of equal strength. Some of these guns were tested by both the Army and the Navy. The smaller calibers stood up well but the larger calibers did not prove successful. This method of construction approached the later idea of the wire-wrapped guns.

The early development of the modern system of hooped guns is traced, through General Fredrix of Belgium in 1830; Thiery of France in 1833; Chamber's American patent for a hooped wrought-iron gun, dated 1849; and the English and American designers, Blakely and Treadwell, in 1855. Between these last two there exists a question as to priority of the principle of initial tension in hooped guns, or of giving to the several layers of hoops such a shrinkage as would cause each to offer its full strength in resisting the action of an interior pressure calculated as the limit for the gun. But very likely we are indebted to the investigations of Lame and Barlow for the origin of this theory and to Rodman, the American, for its exposition.

Chamber's patent, of 1849, embodied: The slotted screw breech; the hinged movement of the breech mechanism, when withdrawn to clear the way for loading through the breech; the loading tray or sleeve inserted in the breech to cover the threads in loading. In design, this gun was a wrought-iron breech-loading smooth-bore built-up gun with a one-piece tube extending from the breech to the muzzle and encased with several layers of hoops shrunk on.

At this time, the most common and the most reliable guns on hand were cast-iron muzzle-loading smooth-bores. The largest gun in service, in 1849, was a 10-inch caliber firing a 125-lb. projectile. The great improvement in the manufacture of cast-iron smooth-bore guns of this period was due to the Rodman method of casting. It may be of interest to note here that at one time Captain Rodman was in command of Watertown Arsenal and it is very probable that he has contributed more to the advancement of ordnance in the United States than any other one man.

In the Rodman method of casting guns, the core or bore was cooled much faster than the exterior layers of metal, thereby causing a hooping effect by the gradual cooling and contraction of the outer layers of metal. This left a condition of stress in the walls of the gun, which was somewhat similar to the condition in the present day built-up gun; that is, the bore was in an initial state of compression while the outer

layers of metal were in an initial state of tension. This also is the earliest example of any type of gun construction approaching the present day cold-working method, which is merely another means of securing an initial compression of the bore. This, however, is secondary to the increase in elastic limit obtained.

A report, dated in 1849, of the first tests of these core-cooled guns states that two 8-in. guns were cast at the same time from the same metal. One was cast solid, as was the usual custom, and one was cast by the Rodman plan. The first gun burst at the 85th round, while the Rodman cast gun endured 251 rounds. An equal and even more convincing degree of superiority was indicated in subsequent tests on 8- and 10-in. guns made in 1851. The condition sought by Rodman finds application today in what we consider the highest principles of gun construction; that is, to obtain an initial state of stress in the walls of a gun so that when the powder pressure acts on the interior, each compound or layer of metal is worked to about the same fiber stress.

The main objection to the Rodman process was its uncertainty. In a number of cases, the castings burst spontaneously upon cooling, and in some cases after the castings were put into a lathe for finishing. In addition, many cavities in the casting were uncovered by boring, causing rejection of the gun as unsafe. Only by mere accident would a perfect state of stress be set up in the gun by this core-cooling process, for the questions of temperature, rates of cooling, thickness of sections, and other variables were determined only very crudely. Several castings were cut into and the initial state of stress determined. Thin rings were cut from the walls of the gun and their contraction or expansion measured carefully and then the state of stress in any section was determined. In theory, it was desired to reach an initial state of tension of about 20,000 lb. per sq. in. or about two-thirds of the averaged resistance of cast iron. In practice, however, it was found that the initial tension of the 10-in. guns varied from 3000 to 28,000 lb. per sq. in. or from 12 to 72 per cent. of the actual tenacity of the iron. These results indicate the uncertainty of the method to produce the results desired. However, at that time, the Rodman guns produced better results than any other type and in 1887 there were 1515 of these guns of major caliber available for land service.

An idea as to the ballistics obtained from the smooth-bores may be obtained from the following: 10-in. round projectile weighs 125 lb.; 10-in. powder charge weighs 25 lb.; 15-in. round projectile weighed 450 lb.; 15-in. powder charge weighed 130 lb.; powder pressure was about 25,000 lb. per sq. in.; range at 20° elevation, 3.75 miles; muzzle velocity, 1700 ft. per sec.

The first system of rifled guns introduced into the United States was called the Parrott; they played an important part in the Civil War.

There were several failures in the larger calibers and they demonstrated the unsuitability of cast iron for rifled guns. These guns remained in service for 25 or 30 years and were gradually withdrawn.

In 1872, a Heavy Gun Board was appointed to meet in New York City for the purpose of examining such models of heavy ordnance as might be brought before it, and of reporting to the Chief of Ordnance such models as might be selected for experiment. The Board examined forty models and inventions and selected nine for trial. They were arranged in order of merit by the Board as follows:

Muzzle-loading gun: Dr. W. E. Woodbridge; Alonzo Hitchcock; cast-iron guns, lined with wrought iron or steel tubes.

Breech-loading guns: Friederick Krupp; E. A. Sutcliffe; Nathan Thompson; French and Swedish system.

Miscellaneous: H. F. Mann; multi-charge (Lyman).

The Ordnance Department was occupied for the next ten years in the construction and trial of these guns. The Krupp's gun was not procured as the War Department did not see fit to comply with the conditions which necessitated the purchase of a number of guns in case the trial gun proved satisfactory. It was intended to test the Krupp breech mechanism with this gun but the breech mechanism was tested later.

The Hitchcock gun was to be made by welding together disks of wrought iron to form a solid 9-in. gun. After three years of work at Springfield Armory, under supervision of the inventor, the project was abandoned as being too difficult and costly to be practicable.

No provision was made in this period for a trial of the French and Swedish systems.

The Mann gun considered by the Board was an 8-in. breech-loading rifle already in possession of the Ordnance Department, which had been fired about 50 rounds.

The Woodbridge gun was a 10-in. wire-wound gun. Doctor Woodbridge first presented his plan to the War Department in 1850, which established his claim to priority for the idea. A 2.5-in. gun constructed by his plan was tested at Springfield Armory in 1865. After 1327 rounds, the firing was stopped because of a defect in the trunnion band, the gun itself being uninjured. The gun decided upon by the Board was a 10-in. muzzle-loading rifle consisting of a thin steel tube strengthened by wire wound on its exterior surface, tube and wire being subsequently consolidated into one mass by a brazing solder melted into the interstices. The gun was completed in 1876. Proof firings were not very convincing and the gun parted longitudinally after 93 rounds. However, the Ordnance Department was impressed with the idea and later made several breech-loading guns with more success.

The cast-iron guns lined with wrought iron or steel tubes were really converted Rodman smooth-bore guns, as the 10-in. smooth-bores were

becoming obsolete on account of the increasing armor thickness of naval vessels. Several guns were tried, using both steel and wrought-iron tubes. The steel tubes appeared to be better and the government placed an order with the Midvale Steel Co. for fifty steel tubes. This was the largest order for steel forgings that had been placed in the United States up to that time. A special grade of steel possessing great ductility was required and the Midvale company supplied the tubes with satisfactory physical properties. Later, tests with the steel-lined guns gave better results than had been obtained before.

Certain tests with converted 8-in. and 11-in. guns, using the Krupp breech mechanism, met with failure, which was the result of a square corner machined in the steel tubes to receive the Krupp breech mechanism. Many people blamed the Krupp mechanism for the failures, but most people, not knowing the true conditions, blamed the failures on the use of steel in gun construction. This opinion was general even among officers of the Ordnance Department. So it was an uphill struggle for several years to prove that the best metal for gun construction was steel.

The Lyman's multi-charge gun was a freak gun. It had very thick walls, which contained pockets along the bore for powder charges; the idea being that as the projectile passed over each pocket, the powder would ignite and exert an additional pressure upon the bore of the projectile. This gun was clumsy and unsatisfactory and was never seriously considered.

The E. A. Sutcliffe gun was a 9-in. breech-loading rifle which essentially was a cast-iron body with a comparatively thick steel tube inserted from the rear and terminating at the front of the blocks. In the rear of the block, the cast-iron body was bored and threaded to receive a hollow, thread-screw sleeve, which supported the block from the rear and through which the charge was inserted. The tests gave no measure of the strength of the system as only 26 rounds were fired, when the project was abandoned on account of a lack of funds.

The Thompson gun was a 12-in. breech-loading rifle. It had a cast-iron body, of the usual Rodman design, in which was inserted under a slight shrinkage a thin steel lining that extended through the bore and was secured by a screw thread at the breech end. It was incomplete when received at the proving ground and in this condition was fired two rounds. A lack of funds prevented further testing.

As for field guns, the Dean 3.5-in. mandreled, bronze gun was procured in 1877 and trials were made at Sandy Hook in 1882. This gun was subjected to a firing test of 50 rounds, which so far as it went, proved the excellent quality of the material; but it was a muzzle-loading gun made after a design already out of date. Also, the introduction and successful use of steel in new construction operated against the extension of the system. This system of manufacture was an early form of the

present-day idea of cold working of metal and is interesting to us for that reason.

The inventor, Mr. Dean, was from Boston and he secured patents on his process in this country, France, England, and Austria in May, 1869. In a report to the Chief of Ordnance, in 1869, he described his experiments showing a gain in the elastic strength, density, and hardness obtained by forcing a series of cylindroconical mandrels, gradually increasing in size, through a hole in a block of bronze 8 in. long, representing the breech of a 12-pounder. The hole, which corresponded to the bore, was increased in size from 2.375 to 2.5 in.; or an expansion of 5.26 per cent. The tensile strength of the metal was increased from 27,238 lb. per sq. in. to 41,471 lb. and the hardness was increased from 1.00 to 2.97.

Many people have been under the impression that this idea of mandreling bronze guns originated in Austria, but official records show that it was not until 1873, or four years later, that Colonel Uchatius of Austria adopted this method for improving bronze guns; undoubtedly, he obtained the idea from Mr. Dean's experiments. In some of the reports of Uchatius, he describes a bore increased from 3.15 to 3.42 in. or an increase of 8.57 per cent., by the same method employed by Mr. Dean.

About 1885, Armament and Ordnance Boards came to the conclusion that the solution of the gun problem was the adoption of a built-up gun of forged steel; also that the industry of making forged steel for such guns should be established. This policy has since been carried out and all the major caliber guns now in service are of either the built-up or the wire-wrapped type.

A few cast-steel guns were made about this time, using a different method for obtaining an initial compression of the bore. A solid cylinder was first cast and cooled. The cylinder was bored out and then heated, and the interior was cooled rapidly, thus securing a small initial compression of the bore. However, the forged steel gun was adopted after a long struggle and results obtained by physical tests, about 1885, show that a good grade of steel was then in use. One of these tests gave the following results: Modulus of elasticity, 30,000,000 lb. per sq. in.; ultimate strength, 90,000 lb. per sq. in.; elongation, 20 per cent.

In Fig. 8, is shown the 16-in., 50-caliber gun firing the first trial shot at an elevation of 20°; the notation underneath this figure may be misconstrued as firing at an elevation of 54° is mentioned, which angle would bring the gun much higher than shown in this picture—54° is the elevation to which the gun must be set to obtain its maximum range of 31 miles.

Charles McKnight, Jr., New York, N. Y. (written discussion).—Not mentioned among the early foundries of the country was the forerunner of the Fort Pitt Foundry. The first iron foundry to be located in Pitts-

burgh and, as far as can be ascertained, the first to operate west of the Allegheny Mountains, was that organized by Joseph McClurg in 1803. A few years later, the firm name was changed to McClurg & McKnight, and still later to the Fort Pitt Foundry. From its inception, it was engaged in ordnance work for the government; and during the war of 1812, guns and cannon balls were made, of which the larger part went to equip and supply Perry's fleet on Lake Erie. This foundry continued to be a source of supply for ordnance, and guns cast here were used in both the Mexican and Civil Wars. During the latter war, the foundry made, according to the president of the present firm, 2038 guns, ranging in size from 4½ to 20 in. The largest of these weighted 116,497 lb. and was designed to throw a 1000-lb. projectile. While the company passed out of the hands of the founders' families, the president and one of the board of directors of the present concern are descendants of the pioneer foundrymen. A few years ago, when excavating in the foundry, a stove plate was uncovered bearing the firm name, the date 1813, and a design symbolical of Perry's victory.

The authors show that after the findings of the Endicott Board were published, about 1885, the manufacture of iron guns ceased. However, those who saw the fighting in France will remember encountering, 1 or 2 km. back of the line where the 75's crouched and sprang like spitting cats, heavy howitzers mounted on obsolescent gun-carriages and manned by the philosophical and bearded reservists, who received with the same stoical shrug the offerings of war and their daily "pinard." Many of these guns had cast-iron barrels and usually were lined partly or in whole with steel tubes, which were rifled. The caliber, most frequently either 190 or 240 mm., went as high as 320 mm., despite which the guns seemed to give good service and stand the stress. These weapons were not modern, and were only used as a last resort when the demand for artillery was enormous and the industrial facilities of the country swamped.

From France also came the newest step in gun construction. During the war, the French ordnance department developed what it called "auto-frettage." By this process, guns are built of one piece (the so-called monobloc construction) and submitted to an internal hydraulic pressure, which expanded the material radially and stressed it beyond the elastic limit so that the metal took a slight permanent set. This, as cold working, resulted in an increased tensile strength, and made hoops and wiring unnecessary. Recently, the publication of our own Ordnance Department suggested that by this method spare tubes for field pieces could be prepared and the pieces retubed in the field, obviating the necessity of a trip to a distant armory for renewal when wear and erosion had used up the old tube.

In concluding, it might be pointed out that the development of the present alloy steel was originally due to the use of alloy steels in guns and

armament. Following Riley's work in 1889, the United States Navy, Sept. 18, 1890, at Annapolis, tried out armor plates, simple and compound, of wrought iron and steel. In this test, the steel plates containing 3½ per cent. nickel submitted by the Schneider (Creusot) firm so far out-distanced all other plates that their adoption by all governments became practically imperative. One authority went so far as to state that by the test the whole British navy was rendered obsolete, as it was at that time protected by a compound plate that proved extremely inferior. The test had just such an effect as did, years later, the launching of the British "Dreadnought."

In the ensuing race for supremacy between gun and armor plate, the guns quickly adopted nickel steel and, under the careful supervision of Army and Navy officers, alloy steel was developed to a continuously higher plane. Thus, with the coming of the automobile, the engineers found at hand the alloy steels, without which self-propelled vehicles would have been almost an impossibility.

Blast-furnace Practice in Alabama

By H. E. Mussey,* Woodward, Ala.

(Birmingham Meeting, October, 1924)

When the American Institute of Mining Engineers visited the Birmingham district in May, 1888, the four Ensley furnaces (Fig. 1) then

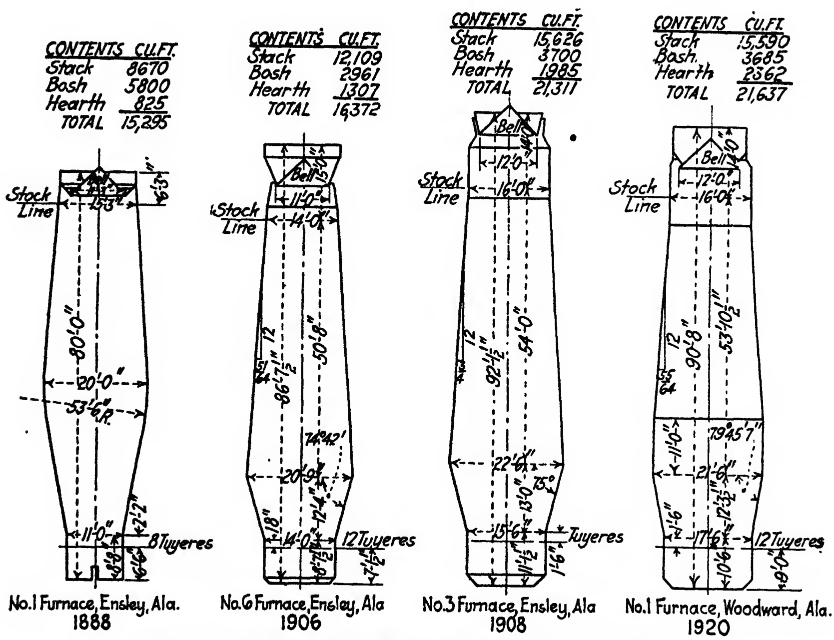

Fig. 1.—Blast-furnace development in Alabama.

completed were referred to as monumental.[1] Their dimensions are given in Table 1. Mr. Gordon stated, with considerable satisfaction, that on the preceding day one furnace had produced 165 tons. The blast was

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* Superintendent of Blast Furnaces, Woodward Iron Co.

[1] Fred. W. Gordon: Large Furnaces on Alabama Material. *Trans* (1888–9) **17**, 135.

22,000 cu. ft., the temperature 1400°, and the pressure varied from 8 to 9 lb. The furnaces continued in operation, with minor modifications

TABLE 1.—*Dimensions of Blast Furnaces in Alabama*

	Four Ensley Furnaces	No. 6 Ensley Furnace	No. 3 Ensley Furnace	No. 1 Woodward Furnace	No. 1 Ensley Furnace
Height of stack, feet	80	86.625	90[a]	89.66	96
Hearth diameter, feet	10.5	14	15.5	17.5	20.33
Bosh diameter, feet	20	20.75	22.5	21.5	25
Stock-line diameter, feet	16	14	16	16	17
Bell diameter, feet	12	11	12	12	13
Bosh angle, degrees	80	74.42	75	79.45	78
Capacity, cubic feet	15,300	16,372	23,211	21,627	31,200

[a] Height from center line of iron notch to top of platform.

from time to time, until the blowing in of No. 6 Ensley, April 26, 1905. The results obtained from this furnace, the dimensions of which are given in Table 1, were so satisfactory that No. 5 was rebuilt to virtually the same dimensions. Later the No. 3 furnace was constructed to the dimensions given in Table 1; the next largest furnace then was the remodeled No. 1 Woodward Iron Co. stack.

During its first year, the following results were obtained from the No. 1 Woodward furnace:

	January	February	March
Average daily tonnage of iron	479	442	469
Average cubic feet of blast	59,520	60,842	62,225
Average pressure, pounds	22	21.7	20.5
Average charge of ore, pounds			
Woodward red ore	27,600	21,886	22,729
Redding	1,734	7,368	5,193
Soft	386	1,000	1,000
Average charge of scrap, pounds	81	121	300
Average charge of coke, pounds	14,000	14,000	14,000
Average charge of stone, pounds	1,728	2,097	1,997
Average number of charges per day	97	92	99
Burden ratio	2.12	2.17	2.08

This shows that the daily output had increased virtually 300 per cent. over the figures given for the plant of 1888. This furnace has been exceeded in size by No. 1 Ensley, the dimensions of which are given in Table 1. The production of this furnace is reported to have reached about 17,000 tons for the month. It would seem therefore that the term "large furnaces" is entirely relative, and that the determination of the ultimate size and shape of the furnace is still in process of solution.

Raw Materials

Iron Ore

The important iron industry that has been developed in the Birmingham District has depended, and will depend on the Clinton iron ore of Red Mountain as a source of ore supply. Regarding these ores, Ernest F. Burchard says:

> The structure and mineralogy of the Clinton ores are closely related features of the deposits. The ore with its associated minerals occurs in lenticular beds analogous to strata of sandstone, shale, and limestone, and interbedded with such rocks.
>
> The fossil ore consists of aggregates of fossil organic forms such as bryozoans, crinoids, corals, and brachiopods. These forms were evidently at one time principally calcium carbonate, and they have been replaced partly or wholly by ferric oxide. The fossil material, much of which consists of broken and waterworn fragments, evidently was gathered by the action of waves and currents into beds, and subsequently cemented together by calcium carbonate and ferric oxide. More or less clay material has been likewise included in the beds during their formation, and this commonly exists as thin seams of shale..
>
> The oolitic ore consists of aggregates of flat grains with rounded edges, somewhat of the size and shape of flaxseeds. These grains generally lie with their flatter sides parallel to the bedding planes of the rock, and the mass is cemented by ferric oxide and more or less calcium carbonate. The flat grains have a nucleus of quartz, generally very minute, about which successive layers of iron oxide and, in many instances, very thin layers of silica and aluminous material have been deposited. One of the two varieties of ore generally predominates in a bed, but in certain localities the fossil and oolitic materials are mixed in nearly equal proportions. The fossil ore, where unweathered, as compared with the oolitic ore in the same condition, is apt to be the more calcareous, while the oolitic ore may carry higher proportions of silica and alumina.
>
> A characteristic of the Clinton ore that is secondary rather than original is that where weathered or acted upon by surface waters the lime carbonate is dissolved out of the beds, thereby increasing the content of iron oxide, silica, and other constituents proportionately. Such altered ore is popularly termed "soft ore," and appropriately, too, for where altered it is usually porous and friable as compared with the unaltered material, which is termed "hard ore." The alteration of the ore beds takes place along the outcrop and to distances of a few feet to 400 ft., depending on the altitude of the beds and on the thickness and permeability of their cover. The quantity of the soft ore is small as compared to that of the hard ore, and owing to its higher content of iron and its greater accessibility, much of the soft ore has already been taken in mining, so that in the future the reserves of this variety of ore will steadily decrease in importance.

It may be stated, in a general way, that the average composition of the ore of a given mine is fairly constant, but the character of the ore changes from the ideal self-fluxing grade, which is in the zone near Reeder's Gap, the silica slowly increasing in the vein, either north or south of that point. A similar variation also occurs in the lime content. Typical analyses, selected from various points along the mountain, are given in Table 2. These analyses represent the "hard ore" as the

remaining "soft ore" represents a comparatively small tonnage and does not occupy the prominent position it did in the earlier days of iron-making in the district. An important step was taken about 15 years ago,

TABLE 2.—*Typical Analysis of Hard Ore*

	Iron, Per Cent.	Silica, Per Cent.	Alumina, Per Cent.	Lime, Per Cent.	Manganese, Per Cent.	Phosphorus, Per Cent.	Water, Per Cent.
Muscoda No. 4 (T. C. I. & R. R. Co.)	34.23	10.59	3.13	19.62	0.16	0.29	0.34
Fossil No. 7 (T. C. I. & R. R. Co.)	36.42	11.71	2.83	17.51	0.17	0.33	0.31
Ishkooda No. 12 (T. C. I. & R. R. Co.)	37.27	16.76	2.94	14.03	0.17	0.38	0.55
Spaulding (Republic)	37.44	21.32	3.31	11.09	0.16	0.30	
Raimund (Republic)	32.32	12.15	3.55	19.52	0.15	0.28	
Woodward	36.76	11.94	3.03	16.93	0.17	0.28	
Redding (Woodward)	39.62	13.60	3.12	13.75			
Ruffner (Sloss)	36.91	21.16	4.47	9.78			

when the ore was much more finely crushed. The standard setup for crushing hard ore would show, approximately, the following screen analysis. The ore is received at the furnace as run of crusher; no attempt has been made to grade by screen sizing.

	Per Cent.
Ore through ¼ in.	37
½ in.	9
1 in.	14
1½ in.	26
2 in.	10
2½ in.	3
3 in.	1
	100

The Red Mountain ore is a hard compact mineral and, as shown by Dr. J. R. Harris, the moisture ranges between 0.5 and 0.6 per cent.; it rarely exceeds 2 per cent. The brown ore, which is a limonite, occurs in clay pits from which it is removed, after stripping the overburden, by means of a steam shovel. The nodules, or lumps, occur embedded in the clay, and the quantity of material removed per ton of ore recovered may range from 2 to 6 tons. The clay is loaded in drop-bottom cars, from which it is dropped into a bin, supplying a log washer. All dornick is passed through a Gates crusher, which reduces it to about 4 in., before passing to the washer. Revolving logs, meeting an adequate supply of

water, tear loose the adhering clay, which is washed away by the current of water. The ore is then discharged from the upper end of the log, after which it drops into a revolving fine screen, where jets of water, under high pressure, remove any remaining clay particles. The analysis of the brown ores is exceedingly variable, even at the same pit. A fair stock-house sample would be represented by the following analysis, although much richer and somewhat poorer ores have been used.

	Per Cent.		Per Cent.
Hydroscopic water	7.00	Alumina	3.61
Combined water	6.00	Lime	0.84
Metallic iron	48.54	Phosphorus	0.38
Silica	11.22	Sulfur	0.09

Flux

The use of limestone as a flux has been virtually discontinued by the furnaces of the district. It is difficult to obtain a limestone low in silica content within a favorable freight zone, and it is believed that a dolomitic slag is preferable for smelting the red hematites, which has resulted in the almost exclusive use of the latter as a furnace flux. Large deposits of dolomite easily available in the district have about the following composition:

	Dolomite A, Per Cent.	Dolomite B, Per Cent.	Rockwood Limestone, Per Cent.
Iron	0.14	0.67	
Silica	0.41	1.20	1.10
Alumina	0.28	0.69	0.93
Lime	31.51	31.48	97.92
Magnesia	20.19	19.74	0.05

The quarry size dolomite is passed through a No. 8 Gates gyratory crusher, which reduces the product to about 4 in. In some cases, the crushed stone passes over a grizzly, which takes out fines below ½ in. These fines are then washed, for the removal of fine material, and the finished product is used in the open-hearth furnaces. In other cases, the run-of-crusher material is sent direct to the blast furnace.

Coke

The coke is made largely in byproduct ovens, of which two types are in use; *i. e.*, Koppers and Semet Solvay. Coke from either is a very satisfactory fuel. The cell volume shows a wide variation, depending on coke-oven practice. For instance, it is possible, with Pratt coal, to develop a coke showing about 33 per cent. porosity, while treated under lower heats, and a shorter coking time, the same coke will develop as high as 53 per cent. porosity. The coke that seems to produce the most

satisfactory results at Woodward is one having a porosity of 42½ to 44 per cent.

It is our practice to screen coke over a ¾-in. grizzly, passing this product over a 7/16-in. revolving screen, the undersize being utilized as fuel under the coal-mine boilers, while the oversize is returned as made to the furnace. Others classify the oversize as "domestic," and dispose of it on the market as such, while the fines are used in the boilers.

The coke is derived from two main coal supplies—the Pratt seam, in the Warrior coal field, and the Big seam. In the earlier days, coke was made from unwashed coal, but the ash and sulfur contents were so high that washers were installed; they are now regarded as a necessity throughout the district. In the case of Pratt coal, the ash content after washing will run from 4 to 5½ per cent.

	Pratt Seam (Woodward), Per Cent.	Big Seam (Sloss), Per Cent.
Volatile matter	1.00	1.61
Fixed carbon	88.70	85.43
Ash	8.71	12.96
Sulfur	1.00	0.80
Phosphorus	0.004	
Porosity	42.3	44.00
Shatter	69.8	

Slag

Typical slag analyses, using dolomite as a flux, when making foundry and basic grades are approximately as follows:

	Foundry, Per Cent.	Basic, Per Cent.
Silica	36.90	34.55
Alumina	12.36	11.34
Lime	44.10	45.60
Magnesia	4.52	6.21
Ferrous oxide	0.56	0.77
Sulfur	1.56	1.53

The slag is disposed of by means of the standard slag ladle, and, after solidification, is marketed as ballast or concrete material. A very small tonnage is granulated and used in the manufacture of cement.

Pig Iron

The product of the furnaces may be roughly divided into two divisions: The first would include the various grades of foundry iron, while the second would represent the steel-making or basic iron. For many years, the output was confined to foundry grades only; but during 1895, the Tennessee Coal, Iron & Railroad Co. secured an order from the

Carnegie Steel Co. for a trial lot of basic iron. This experiment demonstrated that basic iron could be successfully made from Birmingham ores and resulted in the erection of a small, experimental, steel plant, which produced a satisfactory open-hearth product and which was later followed by the larger steel plant at Ensley. The district, from that time, has continued to produce basic iron, not only for home consumption but for the Northern markets. Ferromanganese, also, is produced in one or more of the local furnaces. A low-phosphorus iron, known as ingot-mold iron, is also made from a mixture consisting almost entirely of steel scrap; this product finds a local use at one of the steel mills but is not offered as a market product.

Stock Distribution

With the increasing size of furnaces, the hand-filling method had to be abandoned and a number of mechanical tops have been installed, with more or less success. Perhaps the Brown top, as installed at Ensley No. 6, in 1905, represented the introduction of the more modern type, although there were some in the district prior to that time. The life of the lining was not regarded as satisfactory, and the cost of maintenance and loss of time because of frequent repairs led to the development of the Crockard top, which is now installed on the six Ensley and the three Woodward furnaces. The Woodward furnaces (Fig. 2) are single-skip furnaces, whereas those of the Tennessee company are double-skip. For this reason, the Woodward tops, while representing a simplified form of construction over the original Ensley tops, must provide movable deflecting plates over the upper bell, to minimize segregation, which is not strongly in evidence with the double-skip top. These baffle plates, on either side of the central bell rod, split the charge on the principle of the well-known sample riffle. Between skips, each baffle is automatically rotated 90°, and a half skip load is then directed to alternate quarters of the furnace, thus avoiding the possibility of any section receiving an excess of fines. The rotation of the baffles (Fig. 3) is effected by small steam cylinders, which are interlocked with the little bell cylinder, making the operation automatic. The mechanism has proved very satisfactory and requires no other attention than the periodic replacement of the wearing plates. The spout of the distributer moves through 64° per skip trip.

No. 3 Ensley furnace, operated with this top, produced on its first lining 1,429,788 tons, which is probably a world record. In producing this tonnage of iron, probably about 6,148,000 tons of material passed through the furnace. No. 2 furnace, a sister stack, blown in shortly thereafter, produced 1,196,000 tons. No. 2 Woodward was equipped with this type, and blown in Oct. 7, 1921. The production to date is 397,543 tons of iron, with every indication of an indefinite run, as the

pyrometer readings recorded daily in the upper stack section show little change in temperature over that of the first month's operation.

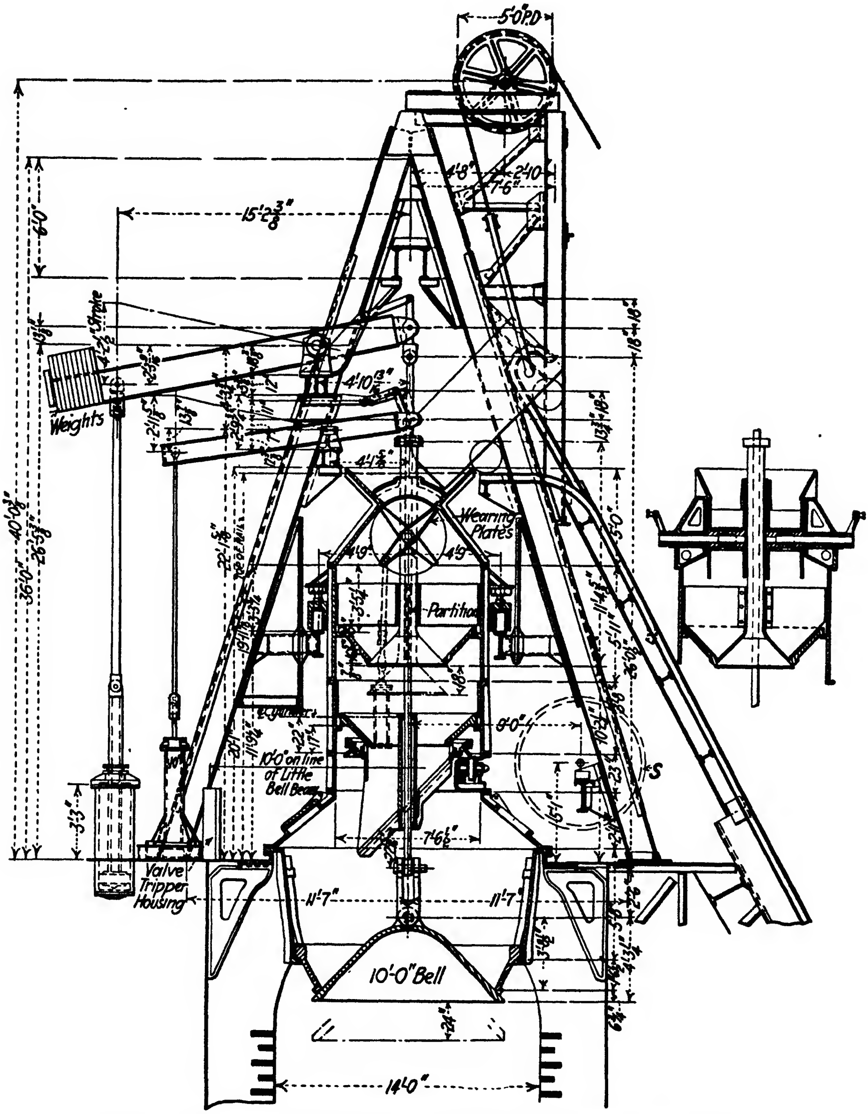

Fig. 2.—Side elevation of top for No. 3 Woodward furnace.

The Pioneer furnaces of the Republic Iron & Steel Co. are equipped with modified McKee tops, which were installed some years ago. The later design may be seen at the North Birmingham furnaces of the Sloss-Sheffield Steel & Iron Co.

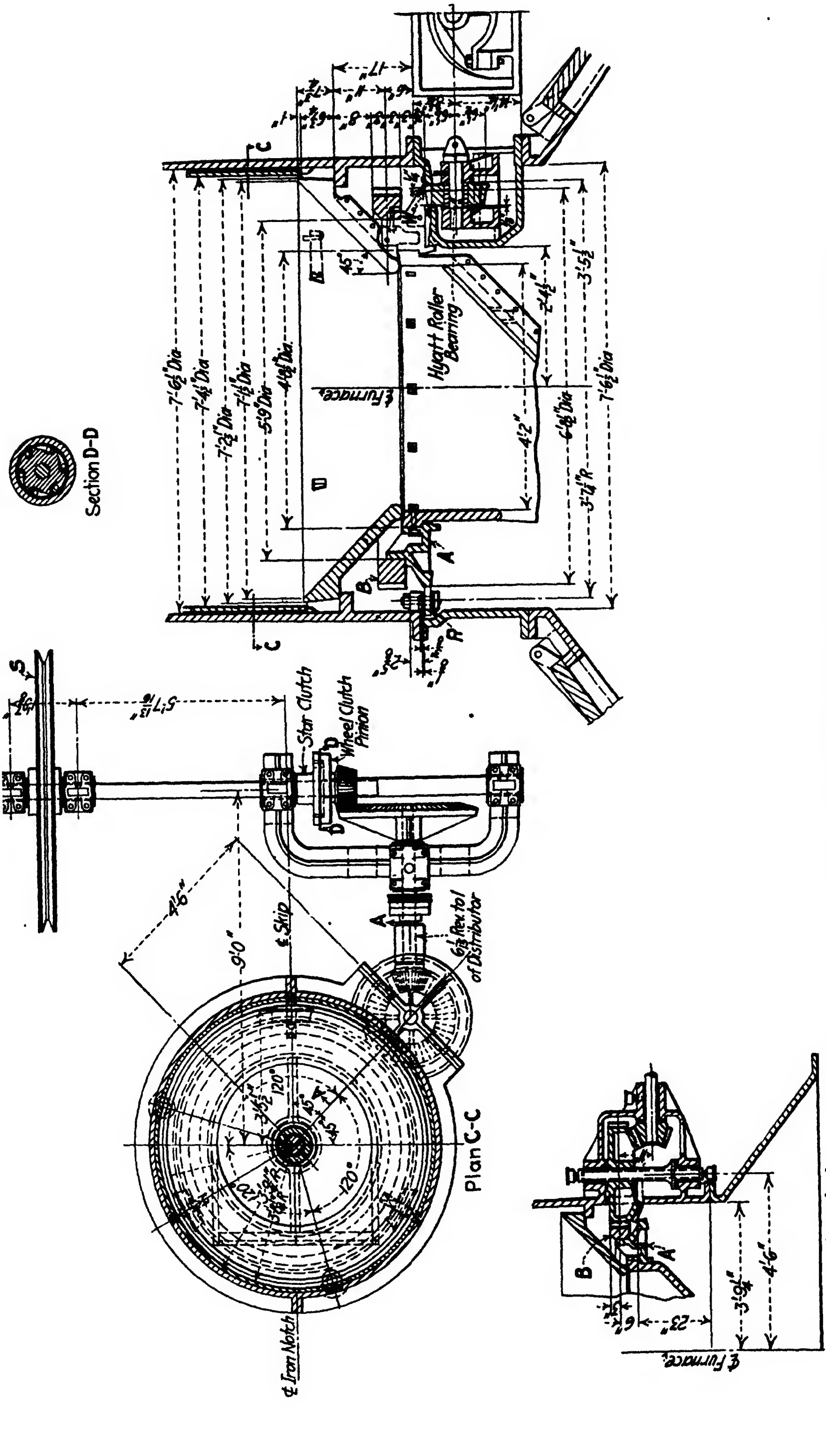

FIG. 3.—DISTRIBUTER TURNING MECHANISM FOR TOP NO. 3 WOODWARD FURNACE.

Thickness of Lining

The stack lining has varied from 9 in., in the case of the water-cooled jacket of the thin lining, to 54 in., with the solid heavy wall type. Our practice carries a 40½-in. wall, with an inwall batter of 55/64 in. The stock line is protected with cast-iron plates (low silicon and high sulfur) embedded in the brickwork. These plates are spaced vertically 9 in. apart, for a distance of 8 ft. in the throat. These blocks are 3 in. thick, and 22½ in. wide, and run about 12 to a complete circle. The arrangement, which has proved satisfactory, is shown in Fig. 4.

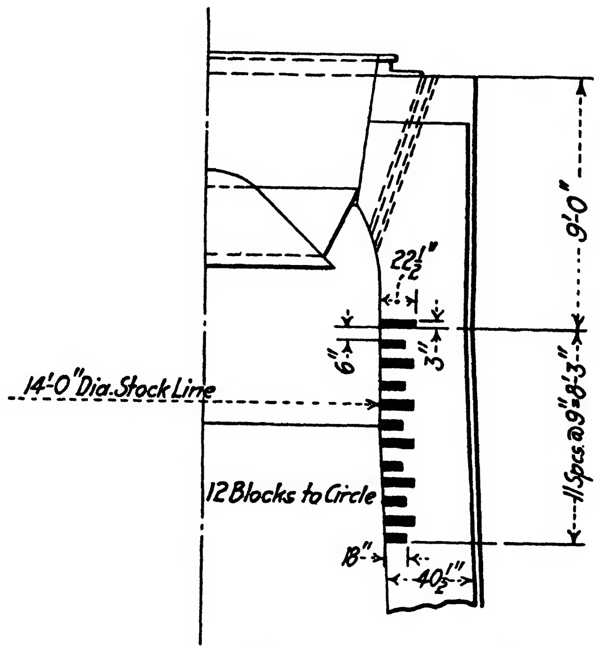

Fig. 4.—Arrangement of stock-line armor.

Bosh Protection

It is the practice, with the larger furnaces, to use the bronze cooling plate in a cast-iron housing. In the rows near the tuyere zone, it has been found necessary to cool the housing by means of a pipe coil. The tuyere zone is protected by a heavy cast-iron or steel "spectacle" belt, strongly banded and linked, and through which at suitable points bronze plates are introduced for cooling those sections between the tuyeres. This construction very satisfactorily resists the severe action of the large slag volumes, with which Southern practice contends.

Hearth Protection

The hearth is enclosed either in heavy iron sections, ranging in thickness from 8 to 10 in., with machined joints, which are held by shrink links and bands, which are cooled by water sprays, or by the thinner cast-steel sections, usually 4½ in. thick, which are held by machined bolts and bands. Wells are either wet or dry.

Dust Catchers

The satisfactory dust catcher constitutes an unsolved problem. The usual primary dry dust catcher is sometimes supplemented by one or

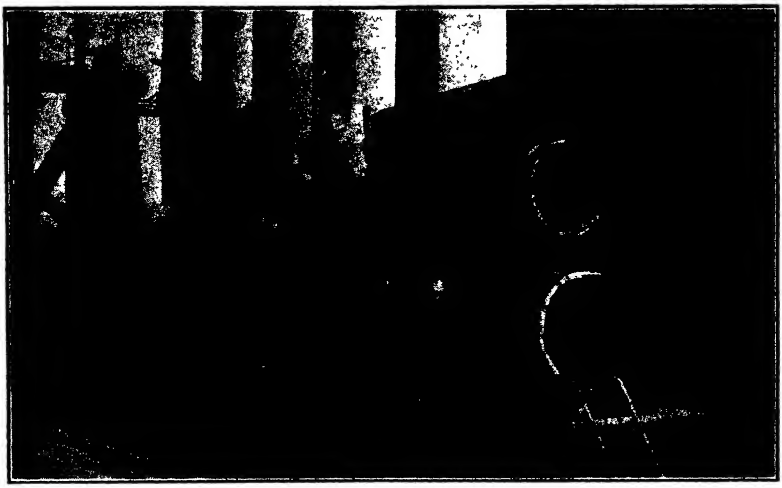

Fig. 5.—Dovel gas cleaner.

more dry dust catchers in which separation is effected by current reversals. The Mullin washer has been used at several plants and unquestionably removes a large quantity of dust that passes the primaries. The loss in sensible heat is not appreciable.

A form using a relatively small quantity of water and not greatly reducing the temperature has been developed by Mr. Dovel, gen ral superintendent of the Sloss furnaces; it is shown in Fig. 5. This cleaner has a maximum diameter of 9 ft., is 74½ ft. long, and is set with a fall of ½ in. per ft. There are two parallel longitudinal troughs, over the center of which are placed two baffle plates. The centrifugal action of the gas throws the dust into these troughs, while a stream of water continuously removes the deposited dust. A test made at the City furnaces of the Sloss company showed a dust content in the raw gas of 7.34 gr. per cu. ft.; after passing through the cleaner the gas carried 0.59

gr. The average flow of gas was 43,920 cu. ft. per min. The average temperature drop was 43°, representing a loss of 12.9 per cent. of the total sensible heat; 310 gal. of water were circulated per minute. Mr. Dovel, in a personal letter, advises that "one set of these stoves had 4½ years continuous service, at high temperatures, and they are ready to start another blast without any repairs whatever." This cleaner is now in service at eleven furnaces.

Several dust catchers of the whirler type have also been installed. Due to the comparative scarcity of water, it has not been possible to install any of those types in which large volumes of water are necessary for the successful removal of dust and moisture.

Stoves

Stove types are as numerous as the furnace plants. They include the two-, three-, and four-pass types. The most recently constructed stoves are 22 ft. in diameter and 110 ft. high; they are of the two-pass type. High heats are desired and 1400° to 1500° has been carried only because the stoves would not permit higher temperatures.

Stock Yards

The stock yards are much simpler than those of the Northern plants; first, because of the milder winter climate, and, second, the furnaces are

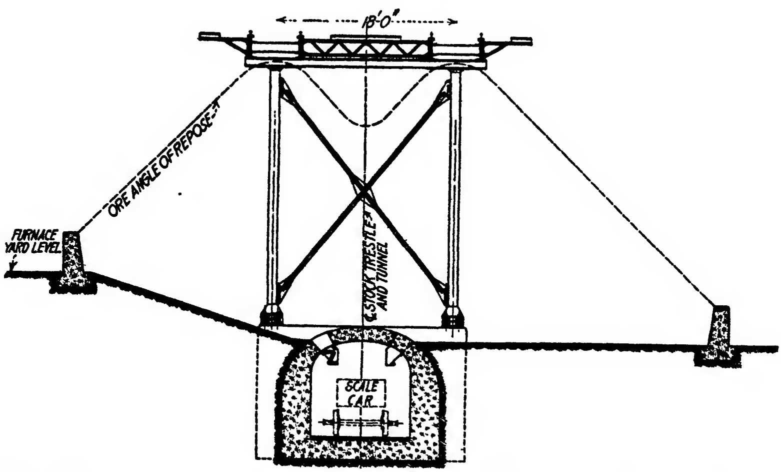

Fig. 6.—Cross-section through stock trestle, Woodward tunnel system of ore storage.

near the ore supply. Where space is available at the ore mines, it is an easy problem to stock large piles from which recovery may be promptly made by steam shovel into the ore cars, which reach the furnace in a few

hours. Fig. 6 shows an interesting stock-yard development made by A. H. Woodward, chairman of the Woodward Iron Co. This plan, which commends itself for simplicity and low cost of installation and maintenance, may be found at Woodward, at the North Birmingham furnaces of the Sloss company, and the Pioneer furnaces of the Republic Iron & Steel Co. Other installations have been made outside of the district. There is only one stock-yard gantry crane in the district.

Cast House

Most of the foundry furnaces run the cast into either sand or chill molds. The molding machine described below[2] is in use at the Woodward furnaces. It is shown in Fig. 7.

Fig. 7.—Pig bed molder.

After the previous cast has been removed, the bed is thoroughly wetted down by an overhead spray system that is easily controlled and that gives a uniform soaking to the sand bed. This wetting puts the sand in proper condition for molding and incidentally exposes any pieces of iron or scrap on the surface of the sand. These are removed before the operation of harrowing.

[2] F. J. Crolins: Straight Line Production. *Blast Furnace and Steel Plant* (1924) 12, 267.

The harrow consists of a rectangular frame having an 8-in. double, extra heavy pipe for the front member, a 90-lb. rail for the rear member, with two side members of ¾ by 6-in. flats bent in the form of sled runners; these prevent the teeth from digging too deeply into the sand. The teeth bolt through the 8-in. pipe at 5-in. spaces and are set to loosen the sand to a depth of 9 to 12 in. The rail rear member smooths the bed and helps to grade the bed to desired level. About two trips are made over the entire length of bed with the harrow, which is the same length as the width of the bed. The harrow is dragged through the sand toward the furnace and carried back over the sand by the cast-house crane.

The roller is now dragged over the sand leaving a series of perfectly molded imprints of pig bed and sow, each identical with the others and exactly spaced. The roller is not truly cylindrical but is more nearly a four equal-side figure whose sides

FIG. 8.—DOVEL PIG BREAKER.

are cycloids. Each side comprises a bed and carries a sow mold running the whole length with 28 pig molds attached thereto. The pig molds are so formed as to leave a minimum neck joining the pigs to the sow and to form a notch in center of pig to facilitate its being broken.

After the roller has traversed the length of cast steel, the bed is ready for the cast, the only hand work necessary being to connect the sows at their ends to the runner.

Pig roller iron is smoother, freer from sand, and more uniform in size than that made in hand-made beds. The individual pigs are a little lighter. For these reasons, foundries prefer it to the old type of pigs.

The bed of pig iron or "comb" is picked up by electric cranes, and delivered to a Ladd & Baker pig breaker, from which the broken pig and

sows drop by gravity into gondolas. A somewhat simpler form of pig breaker, but one of much less capacity, is the Dovel breaker (Fig. 8) at the North Birmingham furnaces of the Sloss company. In this case the "comb" is laid upon a cast-iron breaking bed, while the air-operated hammer is traversed by means of the crane. In some of the latter plants, the breaker is set high enough to permit the installation of screens, which remove the sand that would otherwise drop into the car.

Summary

In briefly summarizing the practice of the district, it may be stated that Southern practice is disposed to carry higher stove temperatures than Northern plants, also, the blast volume for a given size of stack is higher. It has been found necessary to overblow Southern furnaces, compared with Northern furnace practice, if the same relative maximum tonnage is to be realized. Increased production may be expected as a result of even larger furnaces than those now classified as large furnaces.

Furnace lines are still being modified to proportions that are not at present regarded as the ultimate or final form. With the more thorough cleaning of the gas and adequate stove capacity, still higher average stove temperatures will be maintained, resulting in lower fuel consumption and therefore increased production. With the high humidity, as for example during portions of last July, when moisture content reached 13 gr., such conditions may warrant the installation of dry blast plants.

DISCUSSION

C. A. Meissner, New York City.—In 1890 when the furnaces were small it was quite hard with these lean ores to obtain a output that would approximate the same output in the North. Of course, conditions vary somewhat, where you make basic iron, and other branches. We could easily run the temperature of our Northern furnaces up to 1200° to 1400°, but our ores will not stand it while your ores do.

I want to find out later how some of the different gas-cleaning processes are operating. The Dovel process seems to be successful and simple, and there are other processes that seemed to be successful or partly successful. Dry cleaning is a great advantage, as the material is left in condition to be easily handled. The difference between the dry and wet cleaning lies mainly in the fact that wet cleaning leaves the material in a condition that is bad to handle. If we could have dry cleaning at all these plants, as well as the plants in the North, it would make a great difference in the handling of the products. The flue dust is leaner than up North, it contains less iron, and more coke and, therefore, is not as valuable.

The Crockard furnace top is a modification of the Brown top. In the North, the question comes up "Had we better try to work with a stationary top or with a removable top?" Many of our furnaces are equipped with stationary tops and do very good work, others have the McKee tops. Some operators prefer one kind and some another. I think the general belief is that the rotating top gives the best distribution but no practice, of course, will apply to all plants alike.

As it takes about 3 tons of your ore to produce 1 ton of pig iron while up North the proposition is about 2 tons to 1 ton of pig iron, you must handle large slag volumes, and I wonder sometimes if that has anything to do with the heat you can carry.

Franklin H. Crockard, Birmingham, Ala.— My experience has been that the smaller furnaces burn a great many fewer tuyeres than the larger furnaces; that is, on the same coke and ore. I am inclined to think the fusing line in the larger furnaces has something to do with it. In our furnaces, the ratio of tuyeres burned is identical with the size of the furnace.

H. E. Mussey.—In regard to the number of tuyeres burned, it is my observation that more tuyeres are burned when the furnace is going from hot iron to cold iron, or from cold iron to hot iron, than when making uniform grades. The explanation of this is probably due to the change of the fusion point.

As to quality of coke, my experience is that we get the best practice and carry most burden when the coke has a porosity of about 42. The main reason for this low porosity of coke is that with our low-grade ores it is necessary to put a great deal of stock through the stack; to accomplish which we must blow a great deal more wind than is the case in the North—the low porosity coke enables us to do this.

As to the size of the furnaces, I believe that the limit has not been reached. With large furnaces, it is necessary to blow a great deal more wind than is the case with the small furnaces, and the size of the furnaces will be determined by our ability to get sufficient stove heat to back up the wind.

The largest furnace in the district is No. 1 Furnace, Ensley, which has a hearth diameter of 20 ft. a bosh diameter of 25 ft., and a content of about 32,000 cu. ft. This furnace is making about 600 tons of mill iron at the present time on about 2600 lb. of coke per ton of iron. Inasmuch as the furnace labor will cost about the same for a 300-ton furnace as for a 600-ton furnace, the operating cost per ton of iron on a 600-ton furnace is about 50 per cent. of the cost on a 300-ton furnace, so that the larger you can build the furnace and still maintain an economical practice, the cheaper the product will be.

The general lines of furnaces with regard to the bosh have changed materially from the old days; when they used brown ore largely in the burden, the bosh ran up from 20 to 30 ft. above the tuyeres, while in the present furnace, the bosh is only from 10 to 15 ft. in height.

W. H. OLDHAM, Fairfield, Ala.—In 1907, I took charge of Alice Furnace of the Tennessee company. There was but one blast furnace at this place. The work was much more difficult than it is today, as the raw materials were poorly prepared and more difficult to get to the furnace. As time has passed we have developed or improved the raw materials. Also the tops of the mechanically filled furnaces at Ensley have been very much improved; these two things have enabled us to operate furnaces much more uniformly. There have been improvements caused by better knowledge of handling the volume of wind blown, this being perhaps one of the greatest developments in the practice in this district. For example, if the furnace was producing 300 tons of pig iron per day and you were expecting 375 or 400 tons out of the furnace and the furnace was capable of producing that tonnage, in the early days, it was difficult to get sufficient wind on the furnace to produce the tonnage. Usually when you increase the wind, after reaching approximately 300 tons, the tendency is for the furnace to blow through when slowly increasing the wind; we found that when we would jump what we term the "critical wind zone," we jumped 8000 or 10,000 cu. ft. at a time, causing the furnace to work down uniformly instead of by jumps or slips. Then we would have a uniform working condition that would give greater regularity with increased volume of wind and a more uniform product. A good size book could be written on improvements in blast-furnace practice in the Birmingham district.

Effect of Sulfur on Blast-furnace Process*

By T. L. Joseph,† Minneapolis, Minn.

(New York Meeting, February, 1925)

Charcoal was the predominant blast-furnace fuel until 1838, when it was found, by the operation of a 2-ton experimental furnace, that anthracite could also be used. This information was a stimulus to the iron industry, particularly in eastern Pennsylvania where anthracite was available at low cost. The production of anthracite pig iron increased steadily and, in 1855, its tonnage exceeded that of charcoal iron. Of the 680 furnaces in operation in 1874, the 226 using anthracite produced nearly one-half the total tonnage. In 1869, the production of coke furnaces exceeded that of charcoal furnaces and, in 1875, coke surpassed anthracite as a metallurgical fuel. In 1907, the output of anthracite pig dropped well below a million tons and its present significance is largely historical. In recent years, the production of coke has gone hand in hand with the production of pig iron and it has gradually attained the position it now occupies as a universal blast-furnace fuel.

Charcoal, however, has great merit as a blast-furnace fuel chiefly because of its freedom from ash and sulfur. The harmful effect of the latter and the necessity of keeping the percentage of this element in pig iron at a minimum are well recognized. Other contaminating elements can be reduced to specified limits in the steel-making process, but the control of sulfur belongs essentially to the blast furnace. The purpose of this paper is to point out the distribution of this impurity in blast-furnace materials and to indicate how its presence alters the composition, quantity, and free-running or critical temperature of the slag, and the relation between these factors, fuel economy, and the cost of iron.

Sulfur Distribution in Materials

Table 1 shows the distribution of sulfur in charcoal practice. Similar figures taken from coke practice are given in Table 2. These data were

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† Metallurgist, North Central Station, Bureau of Mines.

furnished through the coöperation of a number of steel companies[1] and producers of pig iron. It is evident that, although there is very little sulfur in the materials used in charcoal furnaces, about two-thirds of it comes from the charcoal and about one-third from the ore. The amount coming from the stone is negligible. Approximately 33 per cent. of the total sulfur charged enters the metal, while in coke practice this same value is less than 5 per cent.

TABLE 1.—*Sulfur Distribution per Ton of Iron in Charcoal Furnaces*

Number of Furnace	Pounds Sulfur in Ore	Per Cent. Total Sulfur from Ore	Pounds Sulfur in Charcoal	Per Cent. Total Sulfur from Charcoal	Total Sulfur* Charged	Pounds of Slag	Per Cent. Sulfur in Slag	Pounds Sulfur in Slag	Per Cent. Total Sulfur to Slag	Pounds Sulfur in Metal	Per Cent. Sulfur to Metal	Pounds Sulfur Unaccounted for	Per Cent. Sulfur Unaccounted for
1	0.61	48.8	0.64	51.2	1.25	546	0.10	0.55	44.0	0.45	36.00	0.25	20.00
2	0.33	33.7	0.65	66.3	0.98	498	0.11	0.55	56.1	0.29	29.60	0.14	14.2
3	0.42	33.0	0.85	67.0	1.27	588	0.10	0.59	46.5	0.34	26.80	0.34	26.70
4	0.42	32.0	0.89	68.0	1.31	548	0.09	0.49	37.4	0.45	34.30	0.37	28.30
5	0.47	31.1	0.56	68.9	1.51	500	0.14	0.70	46.4	0.44	29.10	0.37	24.50
6	0.29	35.0	0.54	65.0	0.83	498	0.09	0.45	54.2	0.34	41.00	0.04	4.80

* Sulfur in stone negligible.

Table 2 shows that for each ton of metal made in coke practice an average of 1.38 lb. of sulfur is charged with the ore, 19.9 lb. with the coke, and 0.33 lb. with the stone. Approximately 92 per cent. of the total sulfur charged enters with the coke, 7 per cent. with the ore, and 1 per cent. with the stone. Most of the sulfur is disposed of by means of the slag, which carries off an average of 86.7 per cent. of the sulfur charged, 4.63 per cent. being incorporated into the metal. In a number of cases the sulfur in the slag and metal exceeds the total sulfur charged. These discrepancies are probably due to difficulty in obtaining representative samples and partly to errors in chemical analyses. However, the conclusions concerning the value of coke as its sulfur content varies and, which will be given later, are based on relations existing between three operating quantities, namely, sulfur in the coke, slag volume, and coke consumption. The item, sulfur unaccounted for, contains the accumulated errors of calculations involving the weights of all raw materials per ton of metal and the analysis of raw materials and products. Values used throughout for slag volumes have been calculated by two methods, the accuracy of which depends largely on the magnitude of errors in sampling and chemical analysis. In a few cases the final result may

[1] The writer wishes to acknowledge the coöperation of the following companies: Bethlehem Steel Corpn., Brier Hill Iron & Coal Co., Buffalo Union Furnace Co., Colorado Fuel & Iron Co., Jones & Laughlin Steel Co., Illinois Steel Co., Lackawanna Steel Co., National Tube Co., Republic Iron & Steel Co., Rogers Brown & Co., Youngstown Sheet & Tube Co.

TABLE 2.—*Sulfur Distribution per Ton of Iron in Coke Furnaces*

Furnace Number	Pounds Sulfur in Ore	Per Cent. Total Sulfur from Ore	Pounds Sulfur in Coke	Per Cent. Total Sulfur from Coke	Pounds Sulfur in Stone	Total Sulfur Charged	Pounds of Slag	Per Cent. Sulfur in Slag	Pounds Sulfur in Slag	Per Cent. Total Sulfur to Slag	Pounds Sulfur in Metal	Per Cent. Sulfur to Metal	Pounds Sulfur Unaccounted for	Per Cent. Sulfur Unaccounted for
1	0.89	2.90	28.90	94.5	0.78	30.57	1366	1.62	22.12	72.35	0.78	2.55	+ 7.69	+25.10
2	2.10	1.27	14.25	85.5	0.24	16.59	911	1.43	13.00	78.40	0.76	4.58	+ 2.83	+17.02
3	0.89	3.36	24.80	93.5	0.81	26.50	1389	1.74	24.20	91.30	1.10	4.15	+ 1.20	+ 4.55
4	1.28	8.20	13.95	89.9	0.22	15.45	798	1.70	13.55	87.70	0.85	5.49	+ 1.05	+ 6.81
5	0.88	3.35	24.60	93.7	0.76	26.24	1467	1.81	26.50	100.99	1.10	4.19	− 1.36	− 5.18
6	0.39	2.19	17.10	96.3	0.25	17.74	905	1.30	11.80	66.50	0.69	3.89	+ 5.25	+29.51
10	0.65	3.55	17.40	95.0	0.25	18.30	943	1.59	15.00	82.00	0.54	2.95	+ 2.76	+15.05
15	0.22	1.85	11.50	96.0	0.25	11.97	921	1.38	12.70	106.09	0.45	3.76	− 1.18	− 9.85
16	0.22	1.80	11.80	96.3	0.23	12.25	1062	1.33	14.10	115.10	0.81	6.61	− 2.66	−21.71
23	2.26	12.77	15.20	86.0	0.21	17.67	922	1.67	15.40	87.16	1.10	6.22	+ 1.17	+ 6.62
24	2.90	16.55	14.60	82.5	0.20	17.70	978	1.38	13.50	76.30	1.19	6.72	+ 3.01	+16.98
25	2.38	14.10	14.30	84.7	0.20	16.88	753	1.75	13.17	78.00	0.72	4.21	+ 2.99	+17.79
26	3.78	18.61	16.35	80.5	0.17	20.30	1061	1.65	17.50	86.20	0.96	4.73	+ 1.84	+ 9.07
32	2.20	11.65	16.41	87.7	0.21	18.82	952	1.73	16.46	87.50	0.75	3.98	+ 1.61	+ 8.52
33	2.53	15.30	13.85	83.7	0.18	16.53	852	1.87	15.95	96.50	0.63	3.81	− 0.05	− 0.31
34	1.74	8.88	17.66	90.1	0.20	19.60	893	1.47	13.13	66.95	1.43	7.30	+ 5.04	+25.75
48	1.85	9.88	16.66	88.8	0.24	18.75	1034	1.27	13.13	71.00	0.78	4.16	+ 4.84	+24.84
49	2.47	14.56	13.94	83.8	0.22	16.63	977	1.35	13.19	79.30	0.83	4.99	+ 2.61	+15.71
50	2.10	10.05	18.59	88.9	0.22	20.91	1044	1.36	14.20	67.90	0.92	4.40	+ 5.79	+27.70
9	1.41	7.93	16.15	90.8	0.22	17.78	907	1.83	16.60	93.42	0.92	5.17	+ 0.26	+ 1.41
12	1.36	8.06	15.30	90.6	0.21	16.87	784	1.84	14.40	85.40	0.65	3.85	+ 1.82	+10.75
11	0.42	2.40	16.82	96.0	0.27	17.51	985	1.22	12.02	68.60	0.67	3.82	+ 4.82	+27.58
42	1.32	5.62	21.80	92.8	0.35	23.47	1174	2.24	26.30	112.05	1.41	6.02	− 4.24	−18.07
43	0.83	3.35	23.70	95.6	0.26	24.79	873	2.27	19.81	80.00	1.12	4.52	+ 3.86	+15.48
21	1.05	3.12	32.20	95.8	0.35	33.60	1335							
22	2.86	9.10	31.40	91.0	0.23	34.49	1140	2.00	22.80	66.15	0.45	1.31	+11.24	+32.54
29	0.71	2.76	24.78	96.1	0.27	25.76	1238	2.26	28.00	108.69	2.04	7.92	− 4.28	−16.61
30	0.45	1.76	24.40	96.9	0.31	25.16	1212	2.13	25.80	102.14	1.08	4.29	− 1.72	− 6.43
31	1.63	5.94	25.53	93.0	0.29	27.45	1216	1.85	22.50	81.96	1.41	5.14	+ 3.54	+12.90
27	0.35	1.07	31.82	97.5	0.45	32.62	1676	2.30	38.50	118.02	0.69	2.11	− 6.57	−20.13
39	1.13	3.10	35.00	95.7	0.41	36.54	1505	1.90	28.60	78.30	0.74	2.02	+ 7.20	+19.68
40	2.17	6.84	28.65	90.2	0.93	31.75	1395	1.64	22.90	72.15	0.69	2.17	+ 8.16	+25.68
35	0.31	1.77	16.75	95.8	0.41	17.47	1373	1.11	15.25	87.30	1.21	6.93	+ 1.01	+ 5.77
36	0.31	1.91	15.51	95.4	0.43	16.25	1416	1.18	16.70	102.76	1.39	8.56	− 1.84	−11.32
38	0.30	1.91	14.98	95.5	0.40	15.68	1296	1.14	14.80	94.40	0.78	4.97	+ 0.10	+ 0.63
Av.	1.38	6.49	19.90	91.6	33.0	21.61	1107	1.67	17.81	86.72	1.16	4.63	1.99	8.64

be in error as much as 10 per cent. A portion of the sulfur that is given as unaccounted for is undoubtedly volatilized. It is important to observe at this point, however, that only 4.61 per cent. of the sulfur charged may be allowed to enter the metal. Every furnace operator should ascertain as accurately as possible the quantity and distribution of the

sulfur involved in his particular practice; this information would be an important step in determining the best methods of desulfurization.

Effect of Sulfur Control on the Slag

In coke practice, the elimination of sulfur is difficult because the allowable percentage of sulfur entering the metal is so small. The quantity of sulfur to be eliminated affects not only the amount of slag that must be carried but also its composition. This, in turn, determines its free-running or critical temperature. When comparing the slag volumes of charcoal and of coke furnaces, allowance should be made for the fact that the quantity of ash in charcoal is small. The average slag volume of 35 coke furnaces is 1107 lb., while the average for six charcoal furnaces is only 530 lb. If desulfurization were essential in charcoal operation, it would be necessary to charge enough limestone so that the ratio of bases to acids would be approximately 1. As desulfurization is unimportant, charcoal slags may have a ratio of bases ($CaO + MgO$) to acids ($Al_2O_3 + SiO_2$) as low as 0.4; 530 lb. of charcoal slag will contain 379 lb. of acids and 151 lb. of bases. To get a neutral slag, it is evident that the slag weight per ton of metal would be double the weight of the acids (379 lb.) or 758 lb.; this indicates a saving in slag volume due to the use of an acid slag. Because of the relatively small amount of sulfur and ash that charcoal contains, Sweetser[2] says, "It is safe to count on a saving of 400 lb. of fuel in favor of charcoal compared with coke."

As has been pointed out, the amount of sulfur to be eliminated by the slag makes it necessary to adjust its composition, as well as its quantity. Slag composition and critical temperature are so closely related that they will be discussed together. Table 3 contains operating data from six charcoal furnaces and includes the results of several thousand pyrometric observations of the slag and metal as tapped from the furnace and of that part of the combustion zone visible through the tuyeres. The slag and metal, which collect in the crucible between casts and flushes, constitute the chief source of heat to that part of the furnace below the tuyeres. The theory that slag having a high ratio of bases to acids will increase its free-running temperature and produce a hot hearth is one of the old principles of furnace burdening. A siliceous slag, such as those used in charcoal furnaces, fuses higher in the furnace than would a more basic slag. It is therefore heated less because of the short time it remains in the preheating zone. The ash from the fuel exerts little influence on either the quantity or the composition of charcoal-furnace slags. On the contrary, the slag in coke practice, as it exists in the fusion zone, is highly basic and remains so until mixed with coke ash released at the tuyeres. That part of the slag derived from the coke ash, liberated in the hottest

[2] Charcoal and Coke as Blast Furnace Fuels, *Trans.* (1909) **39**, 228.

Table 3.—*Operating Data from Charcoal Furnaces*

Furnace Number	Furnace Dimensions: Height, Feet	Furnace Dimensions: Bosh Diameter, Feet	Furnace Dimensions: Hearth Diameter, Feet	Charge: Weight of Material per Ton of Metal: Ore, Pounds	Charge: Weight of Material per Ton of Metal: Charcoal,* Pounds	Charge: Weight of Material per Ton of Metal: Stone, Pounds	Charge: Analyses: Charcoal: Fixed Carbon, Per Cent.	Charge: Analyses: Charcoal: Ash, Per Cent.	Charge: Analyses: Ore: Iron, Per Cent.	Charge: Analyses: Ore: SiO_2 and Al_2O_3, Per Cent.
1	60	12.0		4069	1931	155	75.90	1.32	50.6	10.46
2	60	12.5	6.4	4102	2165	271	74.64	1.00	51.3	8.94
3	60	12.0	7.2	4210	1768	42	79.78	1.03	51.3	9.40
4	70	12.0	7.0	4250	2160	410	75.61	1.70	51.9	8.32
5	60	11.6	6.0	4300	2088	256	77.29	1.26	51.7	8.85
6	62	15.0	10.2	4150	1640	269				

* Bushel of charcoal taken as 20 lb.

Operating conditions

Furnace Number	Wind: Pounds Charcoal per Square Foot Hearth Area per Minute	Wind: Pressure, Pounds per Square Inch	Temperature: Blast, Degrees F.	Temperature: Top, Degrees F.	Temperature: Tuyere, Degrees C.	Temperature: Slag, Degrees C.	Temperature: Metal, Degrees C.
1		4.0	950	350			
2	2.49	3.3	920		1682	1454	1405
3	2.17	4.5	980	450	1611	1485	1413
4	4.37	5.0	1050		1710	1440	1423
5	2.47	4.0	700		1687	1413	1398
6	1.57	5.3	1174	400	1655	1465	1435

Products

Furnace Number	Metal, Per Cent.: Si	Metal, Per Cent.: S	Metal, Per Cent.: Mn	Metal, Per Cent.: P	Slag, Per Cent.: SiO_2	Slag, Per Cent.: Al_2O_3	Slag, Per Cent.: CaO	Slag, Per Cent.: MgO	Slag, Per Cent.: S	Slag, Per Cent.: Mn	Slag, Per Cent.: Fe	Tons
1	1.35	0.024	0.50	0.184	54.78	11.97	22.7	2.64		1.40	1.60	87
2	1.42	0.013	0.55	0.186	43.00	18.55	32.0	2.45	0.11	1.02	0.19	52
3	1.19	0.015	0.62	0.169	46.60	19.00	27.5	3.11	0.11	1.76	0.21	70
4	1.53	0.020	0.48	0.162	46.25	17.00	24.4	9.43	0.09	2.48	0.41	112
5	1.25	0.018	0.54	0.175	47.27	19.10	26.3	2.68	0.14	2.64	0.21	48
6	1.88	0.015	0.93		44.50	17.50	35.8	2.20	0.11			112

part of the furnace, raises the temperature of the final slag. In coke practice, this portion amounts to 20 per cent.; while in charcoal practice it is only 5 per cent.

In the following summary, the temperatures measured at forty-eight coke furnaces are compared with the charcoal temperatures given in Table 3:

Fuel	Tuyere, Degrees C.	Slag, Degrees C.	Metal, Degrees C.
Coke	1708	1526	1472
Charcoal	1669	1451	1415
	39	75	57

These temperatures afford the only readily available means of arriving at what has been commonly referred to as "hearth temperature." It is evident that this expression is indefinite for the hearth is often taken to refer both to the plane of the tuyeres and to the portion of the furnace below this level where the slag and metal collect. It is apparent from these figures that the temperatures of the tuyeres, slag, and metal, in these two cases, show a general relationship to one another, but it is not evident that a decrease in tuyere temperature produces a corresponding reduction in the temperature of the slag or of the metal. Although the average tuyere temperature of charcoal furnaces is only 39° below that of the coke furnaces, the temperature difference is 75° for the slag and 57° for the metal. In his study of critical temperatures, Johnson concluded that the slag controlled the temperature of the metal. The temperature measurements reported here corroborate Johnson's conclusion.

Sulfur, Slag Volume, and Fuel Consumption

It has been pointed out, by a comparison of charcoal and coke practice, that sulfur plays an important role in the blast-furnace process. Operators of course realize the advantage in using materials low in sulfur. It seems worth while, however, to point out the probable cost of the fuel necessary to eliminate about 95 per cent. of the total sulfur entering the furnace. The average slag volume of the thirty coke furnaces in Table 2 is 1107 lb. If desulfurization were not essential, coke furnaces could carry as siliceous slags as charcoal furnaces; this would effect a threefold benefit—a saving in stone, a lower slag volume, and a lower critical temperature. The range of slag volumes of the thirty-five furnaces extends from about 800 to 1700 lb. It might be suggested that a given amount of slag is necessary to proper functioning of the furnace.

It is recognized that furnaces which are run too "dry" may cause considerable trouble if the amount of slag is insufficient properly to maintain the hearth temperature. It is obvious that about 550 lb. of acids is contained in the 1100 lb. of the neutral slags recorded in Table 2.

If sulfur could be ignored, as is done in charcoal practice, a basicity ratio (bases to acids) of 0.4 could be used. Only 220 lb. of bases would be necessary to form this slag and the resultant slag volume would amount to only 770 lb.—a decrease of 330 lb. of slag. In addition to the slag required in fluxing the gangue and coke ash, about 300 lb. of extra slag must be used to eliminate properly the sulfur.

The writer has recently given a relationship which shows[3] that 0.46 lb. of carbon is required to melt 1 lb. of slag; this is equivalent to 0.52 lb. of coke containing 86 per cent. fixed carbon. Aside from the cost of stone, the elimination of sulfur is directly responsible for 150 lb. of extra coke. On a basis of 2000 lb. of coke per ton, this is a 7.5 per cent. increase in fuel consumption and causes a 7.5 per cent. loss of tonnage.

In the manufacture of pig iron, 41,976,171 tons of coke was consumed in 1921. The sulfur in coke cost the resources of the country approximately 3,000,000 tons of fuel during that year; this illustrates the importance of the sulfur problem in present blast-furnace practice; in the future, it will assume greater importance because the use of fuel higher in sulfur content will be necessary. These principles have a direct bearing on the proper valuation of metallurgical coke. They also emphasize the importance of supplying the blast-furnace superintendent with low-sulfur coke if he is expected to operate on a low fuel consumption.

The sulfur balance in Table 2 indicates that most of the sulfur must be removed by the slag. The quantity of sulfur discharged from the furnace, of course, is equal to the product of the slag volume and the percentage of sulfur it contains. The sulfur content of the slag, however, is not a constant. It will depend on the temperature, volume, basicity, alumina, and manganese content of the slag. The temperature, in its turn, depends on a number of operating factors, particularly on the burden and the composition of the slag. A basic slag promotes desulfurization, because it attains a higher temperature and because it is chemically more active as a sulfur solvent. The furnace operator, in attempting to produce low-sulfur metal, has to deal with a large number of interrelated factors and finds it is difficult sometimes to make proper adjustments among them.

Charcoal practice furnishes a good example of slags that are siliceous and at the same time possess little desulfurizing power. These acid slags carry off little more than 40 per cent. of the sulfur present. The sulfur in slags received from five furnaces now in operation averages 0.104 per cent. In view of the complexity of the desulfurization process, records of furnace operation guided by experience and judgment furnish the best available basis for conclusions regarding the relation

[3] How Silica Affects the Cost of Pig Iron. *Iron Trade Rev.* (Jan. 24, 1924), 288.

between the sulfur charged and the amount of slag necessary for its proper elimination.

SULFUR IN FUEL AND SLAG VOLUME

The weight of slag made in producing one ton of pig iron can, in general, be taken as a measure of the sulfur present in the raw materials. If a large quantity of sulfur is to be eliminated, a large slag volume must be carried or the sulfur content of the slag must be high. In adjusting slag volumes, furnace operators bear in mind the maximum quantity of sulfur with which they may have to contend. Operators using high-sulfur coke must guard against higher peak conditions. In individual cases, the maximum sulfur in the coke might be considerably in excess of the average sulfur. In such a case, the slag volume would appear out of

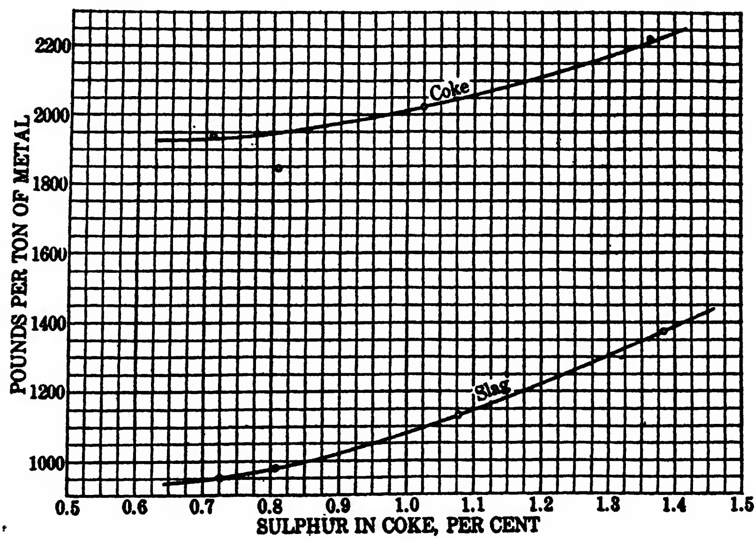

FIG. 1.

proportion with the sulfur in the coke. Operating data from thirty-six furnaces indicate that a rather definite relation exists between slag volume and the percentage of sulfur in the coke. To determine this relation, two factors (slag volume and sulfur in the coke) have been isolated. Thirty-six furnaces were arranged in order of increasing sulfur in the coke, divided into four groups, and the slag volume and per cent. sulfur for the representative groups were averaged. These averages are given in Table 4 and plotted in Fig. 1, each point on the curve representing the slag volume and percentage of sulfur in the coke for nine furnaces. In basing conclusions on relations worked out under actual operating conditions, various factors covering individual practices are taken into

account. The blast-furnace process consists generally of a large number of inter-related factors and it is especially advisable that any conclusions regarding blast-furnace problems have as a background operating data representing a variety of conditions, as well as the judgment and experience of a number of operators.

TABLE 4.—*Relation between Percentage of Sulfur in Coke and Slag Volume*

Group 1				Group 2				Group 3				Group 4			
Furnace Number	Per Cent. Sulfur in Coke	Slag Volume, Pounds	Coke Consumption, Pounds	Furnace Number	Per Cent. Sulfur in Coke	Slag Volume, Pounds	Coke Consumption, Pounds	Furnace Number	Per Cent. Sulfur in Coke	Slag Volume, Pounds	Coke Consumption, Pounds	Furnace Number	Per Cent. Sulfur in Coke	Slag Volume, Pounds	Coke Consumption, Pounds
15	0.61	921	1893	23	0.76	922	1895	10	0.89	943	1952	29	1.20	1238	2067
16	0.61	1062	1932	48	0.76	1034	2193	11	0.89	985	1892	30	1.20	1212	2031
25	0.76	753	1875	38	0.80	1296	1742	6	0.90	905	1907	31	1.20	1216	2129
32	0.76	952	2160	4	0.82	798	1704	17	1.14	1161	1920	28	1.30	1395	2205
34	0.76	893	*	2	0.83	911	1720	20	1.15	1012	2160	22	1.43	1110	2195
50	0.76	1044	*	9	0.83	907	1950	49	1.16	977	1834	27	1.45	1676	2195
33	0.76	852	1955	12	0.83	784	1845	5	1.18	1467	2085	39	1.50	1505	2332
24	0.76	978	1928	36	0.86	1416	1802	1	1.18	1366	2450	40	1.50	1504	2460
26	0.76	1061	1907	37	0.86	808	1736	3	1.20	1389	2070	41	1.50	1616	2462
Av....	0.72	946	1950	Av..	0.81	986	1843	Av..	1.07	1133	2030	Av..	1.36	1385	2230

* Omitted from average because some factor other than sulfur in coke had a marked influence on coke consumption.

It is necessary to carry additional slag when using high-sulfur coke, as the following calculations show. A furnace using 1 per cent. sulfur corresponds, on the curve, to a slag volume of 1100 lb. This quantity of slag would require, according to Fig. 2, a fuel consumption of approximately 2000 lb. This fuel will contain 20 lb. of sulfur. The ore, according to Table 2, will introduce 1.38 lb. of sulfur, making a total of 21.38 lb. charged in the furnace. The sulfur in the stone is so small that it can be neglected. If the sulfur in the pig iron is 0.03 per cent., 0.67 lb. will be incorporated into the metal. A 10 per cent. loss by volatilization will leave 18.57 lb. of sulfur, which must enter 1100 lb. of slag, producing 1.69 per cent. sulfur in the slag. The sulfur in the average slag, in Table 2, is 1.67 per cent.; the maximum sulfur in the slags, as given in the table, is 2.30 per cent. The writer does not wish to give the impression that desulfurization could not be accomplished with a smaller slag volume; for purposes of calculation the average values are more nearly representative.

The lower curve in Fig. 1 shows that as the sulfur in the coke increases, it is necessary to carry additional slag volume. From a study of operating data, the writer has recently developed a relation between slag volume and coke consumption; this relationship is shown in Fig. 2. The upper

curve in Fig. 1 is readily derived, knowing the extra slag necessary for additional sulfur and the coke which, in turn, is required to melt the slag. The actual coke consumptions for each of the furnace groups appearing

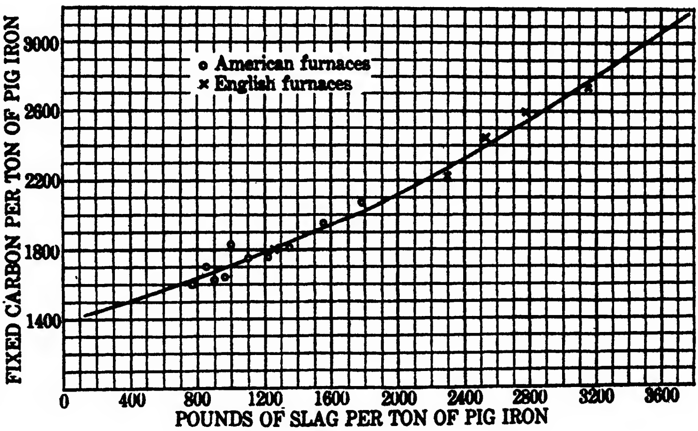

Fig. 2.

in Table 4 are plotted in Fig. 1; the agreement between the points and the curve is shown to be satisfactory.

Sulfur in Coke and Cost of Iron

From these relations a diagram, Fig. 3, has been developed showing the effect that sulfur in coke has on the cost of pig iron. Coke containing 1 per cent. sulfur has been taken as a base line and the change in the cost of making pig iron is indicated for fuel at four prices. The rate of blowing on a 500-ton furnace has been considered constant and a fixed annual charge of $400,000 has been assumed for labor, investment charges, maintenance, repairs, etc. Increased coke consumption with a constant rate of blowing decreases tonnage. The fixed charges have, therefore, been distributed accordingly. The cost of stone at the furnace has been taken as $1.40 per ton and the quantity required taken from Fig. 1. It is now a simple matter to write down the changes in cost of iron made from coke varying in price and in sulfur content. A diagrammatical representation of this, such as appears in Fig. 3, may be of some value.

It is unlikely that means will be found of entirely eliminating sulfur from coke or of preventing its incorporation into pig iron during the blast furnace process. Powell[4] has obtained some interesting information on

[4] A. R. Powell: The Forms of Sulfur in Coke. *Jnl.* Amer. Chem. Soc. (1923) **45**, 1–15.

the forms of sulfur in coke and a more recent study[5] by Powell and Thompson shows the possibilities of desulfurization by steam. An investigation is now under way in the southern district, which involves the removal of stock samples from various positions between the stock line and tuyeres of a commercial furnace to ascertain where sulfurization, as well as desulfurization, takes place. In making a study of the sulfur problem, it is important to know what saving can be made through the use of low-sulfur fuel. Any expenditures made to eliminate sulfur can

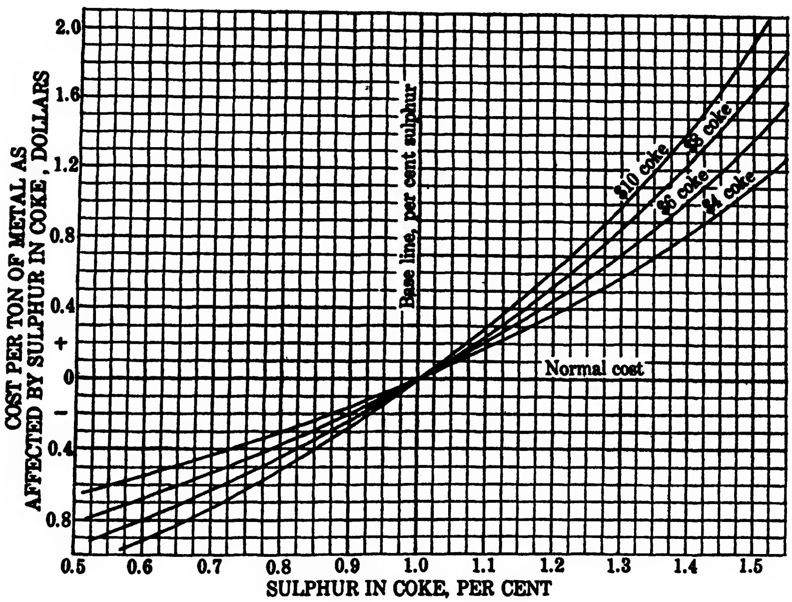

FIG. 3.

only be justified by the increased value of low-sulfur coke. Information concerning the relative value of coke containing varying amounts of sulfur is also of value in directing the development of new coal fields for metallurgical purposes.

DISCUSSION

R. FRANCHOT,* Washington D. C.—One of the interesting points brought out in this paper is the relatively immense weight in the furnace economy of an element present in minute quantity. Of the materials put through the furnace, including the air, sulfur constitutes perhaps

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* Vice-president, Ferro-Chemicals, Inc.

[5] A. R. Powell, and J. H. Thompson: A Study of the Desulfurization of Coke by Steam. *Bull.* 7, Coal-mining Investigations under Auspices of Carnegie Inst. of Technology, Bureau of Mines, and Advisory Board of Coal-mine Operators and Engineers, 1923.

0.15 per cent., by weight, and the author estimates that 7.5 per cent. of the coke is directly chargeable to the sulfur by reason of the increased slag volume involved in sulfur removal. There are grounds for thinking that sulfur is responsible, directly or indirectly, for an even greater proportion of the coke consumption than 7.5 per cent. The author's figure is derived from studies of the variation in coke consumption with variation in slag ratio. It would seem, as sulfur removal is known to necessitate also slag basicity and a high hearth temperature, and as these two factors require the combustion of a certain amount of coke with air, sulfur may account for a greater proportion of the coke than that which can be figured from the increased slag volume alone. For example, assuming 100° C. higher hearth temperature with a 50 per cent. slag ratio at 0.2 specific heat for iron and 0.33 for slag, the additional heat required in the hearth may be taken as 36 pound-calories, or centigrade thermal units, per pound of iron. With a usual blast heat and moisture content and hearth temperature at 1500° C., the hearth-available heat is about 1000 calories per pound carbon burning with air. Hence, each 100° rise of hearth temperature may be estimated to involve 0.036 lb. carbon per pound pig, which with 20 per cent. solution loss and 85 per cent. fixed carbon in the coke amounts to 0.05 lb. coke per pound pig, or 112 lb. coke per ton. The effect of basicity on coke consumption is not readily figured, but the limiting influence of this factor on the burden is well recognized in operating practice, and especially when high silicons are required.

It is interesting to note that the author's empirical constant, 0.45 lb. carbon per pound of slag, for the coke consumed in making slag is, from one point of view, in remarkable agreement with theory. The heating work involved in slag production may be taken to comprise 550 calories per pound as the total heat of slag with 400 calories as the heat absorbed in calcining 90 per cent. of limestone, less 80 calories for slag formation, a total of 870 calories per pound slag as it is made in the furnace. The heat developed in the combustion of coke with air under usual furnace conditions, assuming 600° C. blast heat, 4 grains humidity, and 20 per cent. solution loss, may be estimated at 3280 calories per pound carbon, less 128 calories for moisture decomposition and allowing 630 + 648 = 1278 calories for the deficit of heat due to 20 per cent. solution loss ($CO_2 + C = 2CO - 38{,}880$ calories, leaving a net heat development of 1874 calories per pound coke carbon as charged. It should therefore require $^{870}/_{1874} = 0.464$ lb., carbon to make a pound of slag, a calculated coke ratio that is strikingly concordant with the author's statistical constant.

From the standpoint of the hearth, however, there would not seem to be any such clear theoretical basis for the observed coke consumption in making slag. The heat available at a hearth temperature of 1500° C.

for a 600° blast heat and 4 grains humidity—allowing 2700 calories for the heat carried up in the gases and 650 calories for that brought down in the carbon—is 1102 calories per pound carbon burning with air. With 20 per cent. solution loss, the figure becomes 881 calories per pound coke carbon as charged. A ratio of 0.45 lb. carbon per pound slag indicates 396 calories as the heat available in the hearth per pound slag. This is 72 per cent. of the 550 calories total heat in the slag, and it is clearly impossible that any such proportion of heat remains to be imparted to the slag after it has been in the furnace for from 10 to 15 hr., and has reached the combustion zone.

It seems to be an observed fact that the slag is largely melted well above the combustion zone, and it may possibly be assumed that only the final superheat of say, 200° C. at 0.033 specific heat, or 66 calories per pound, fairly measures the heat absorption in the hearth due to the slag. With such an assumption, a hearth efficiency of 17 per cent. of the theoretical is indicated. In other words, the coke constant may be explained by the necessity of supplying a very small quantity of hearth heat at very low efficiency.

As it may be taken for granted that the low fuel ratio in charcoal furnaces, as compared with coke practice, is to be accounted for by a substantial difference in the hearth conditions, and as it is clear that the introduction of sulfur in the coke not only necessitates an increase of the hearth heat requirements per pound of pig, but also, as pointed out by Johnson, involves a smaller margin of hearth-available heat per pound of coke, and further, as it now appears that the efficiency of utilization of the hearth heat is very low, it may safely be concluded that the sulfur in the coke is a primary underlying factor accounting for the relatively large fuel consumption in coke furnaces.

C. A. Meissner,* New York, N. Y.—Do I understand that you base the amount of slag entirely on the sulfur content of your coke?

T. L. Joseph.—Yes.

C. A. Meissner.—What data have you as to other conditions, such as increased ash in coke, increased silica, etc., in the ore mixtures, that naturally affect the slag production quite seriously?

T. L. Joseph.—Those factors varied. In some cases, the ash in the coke increased with the sulfur; that, perhaps, was the general tendency. It seemed to be a natural condition that the people operating on high-sulfur coke had a high-ash coke and also, perhaps, rather lean ore mixtures. However, increased sulfur in blast-furnace fuel must be eliminated by using a larger slag volume or by increasing the per cent. of sulfur in the slag. We know it is possible, by changing the basicity of the slag, to increase the amount of sulfur eliminated, but the data I have indicate

* U. S. Steel Corpn.

that most blast-furnace men prefer to work with acid slags if possible. They do not like basic slag, so they seem to work very much in the same range as far as the sulfur-carrying capacity goes.

Ralph H. Sweetser,* Columbus, Ohio.—The question of the right kind of iron does not depend on the blast furnace only, it goes back to the coke works and the coal mine. The question of the amount of carbon there will be in the pig iron is tied up with the amount of ash and sulfur in the coal used for the coke for that particular blast furnace.

In blast-furnace practice we lack the evaluations of slag and sulfur and carbon; we have no yardstick for measuring.

The question has been asked, how much control has a blast-furnace man over the carbon? In the past, he had practically no control because he did not know how it got in there. It was my good fortune to have supervision of some tests on blast furnaces a year ago last May, and during the first half of last August, when I was able to get actual temperature of the iron as it came out of the blast furnace with a platinum-rhodium pyrometer, also readings with an optical pyrometer. We believe that the thermocouple records are as near right as can be had.

We found that the lower sulfur coke had lower temperatures for the same composition of iron and had less total carbon, but how much less we are not ready to say. We do not know just how that follows through, but we took the temperature of the iron for two weeks, every cast, night and day; we also took observations every 60 sec. as the iron was running, and many samples of every cast of iron. The observations show that carbon is governed a great deal by the basicity of the slag.

Blast-furnace men try to keep away from basic slag because of the excess fuel it takes. A very limy slag requires much more coke per ton of pig iron than the simple slag. But simple slags will not carry off enough of the sulfur.

I question the statement that 65 lb. of extra slag is required for 0.1 per cent. increase of sulfur. Starting with 2000 lb. of coke and 1 per cent. of sulfur, then 0.1 per cent. of sulfur is going to be only 2 lb. and as each pound of sulfur will require about 3¾ lb. of limestone, that 2 lb. of sulfur will add about 7½ lb. of limestone. There is a connection between the composition of the slag and the calcium sulfide that has not been sufficiently brought out in the investigations, and it will be worth while in a study of the Bureau of Mines to find out the "driving force."

Is there not some "driving" force inside the blast furnace that affects the amount of sulfur, and the temperature and the composition of the slag? Some combination that can be stated as pounds of coke, pounds of sulfur, and going back to pounds of coke.

The question of the elimination of sulfur in the blast furnace must be worked out by the blast-furnace men, the coke-oven men, and the coal

* Assistant to Vice-president, American Rolling Mill Co.

operators, and any one who can evaluate and put it into terms of dollars per ton of coal will do the whole industry a great service.

C. H. Herty, Jr., Lackawanna, N. Y.—As to why 2 lb. of sulfur requires 7 lb. of limestone and 65 lb. of slag, I take it that the sulfur is eliminated in the blast furnace by a reaction something like this; the sulfur in the iron, plus the CaO in the slag form calcium sulfide plus iron oxide.

Is it not true that if we have a slag containing a certain amount of acid in a basic furnace there is going to be a definite ratio between sulfur and slag and sulfur and iron corresponding to a definite basicity, or whatever we want to call it? If we add 2 lb. of sulfur to the iron and 7 lb. of limestone to the slag, we have increased the sulfur in the iron greatly, but we have not increased the basicity of the slag very much. In other words, 7 lb. of limestone going into the slag does not mean a direct increase of 7 lb. of base in the slag. If there is 45 per cent. lime in the slag, the slag is not 45 per cent. basic. The chances are it may be 10 per cent. basic, because most of that lime is held by the silica, and if we add 7 lb. more of the limestone some of it is going to be taken up by silica in the slag, and possibly 10 per cent. of that 7 lb. is going to be free to act on the sulfur. In other words, there must be excess lime over that required to hold the sulfur simply because the basicity of the slag is not determined by the total amount of base in it, but by the ratio of bases to acids. It may be 7 lb. of total base and not free base, and the free base is the thing needed to free the sulfur.

Ralph H. Sweetser.—What has the sulfur to do with the slag? Only enough limestone to take care of the sulfur is to be added; that is 7 lb. is to be added and there are some impurities in the limestone.

C. H. Herty, Jr.—That is the point—silica and limestone combine in any proportion at all. If the temperature is high enough silica and limestone will be fused in any proportion. If a slag contains a definite amount of lime and silica and lime is added the slag will absorb the lime, and as you have a much more weakly held lime it is going to absorb the sulfur. Sulfur and silica are both fighting for the lime; at the same time the lime is fighting for the sulfur and silica.

I. E. Waechter,* New York, N. Y.—The controlling of the carbon content in pig iron is analogous to controlling the carbon in cast iron. Many years ago a German chemist, Wuest, worked out the relationship of carbon to some of the elements. There is a definite relationship between the total carbon present in pig iron and the silicon. In other words, if the sum total of carbon and silicon is a constant value, the higher the silicon the lower is the carbon, and vice versa. It seems to me in those tests silicon ought to be taken into consideration as well as the sulfur.

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F. N. Speller,* Pittsburgh, Pa.—Some years ago we made a thorough investigation of this subject with reference to welding and recorded the results of flange tests on a series of open-hearth heats that ran about 0.06 per cent. sulfur, and another parallel series where the sulfur was forced down to about one-half of that in the previous lot. Each of the tubes was subject to two flanging tests, so that we had a very complete record of these heats. It costs something to remove sulfur, and it appears to be deleterious to the welding quality of steel to force the sulfur below a certain point. The investigation reported by Mr. Herty has been well worked out and contains valuable information. It seems important however, that the reader should not get the impression (which I am sure the author did not intend to give) that it is always desirable to get the sulfur down as low as possible.

T. T. Read, Washington, D. C.—We start with the sulfur in the coke, not in the iron ore; during reduction the sulfur gets into the iron and you must get it out of the iron before you get the iron out of the blast furnace; this is done by a sort of a washing process. The slag is the thing that does the washing. Assuming that the slag is carrying all the sulfur it can, you must have more slag to improve that washing operation sufficiently to take away any extra sulfur and still have the finished iron at the bottom within the tolerable limit.

I. E. Waechter.—In a recent article on the desulfurization of cast iron, Mr. Vile, of the Griffin Wheel Co., tells of a number of experiments made with the desulfurizing compound perfected by some German. He found, by analysis, that this material was very largely (probably 90 per cent.) soda ash and consequently carried out some of his experiments with pure soda ash, which worked almost as well as the compound. The compound was added after the cast iron was drawn from the cupola, and analyses were made of samples taken periodically right from the ladles as they were poured into various castings. The pouring was carried on throughout the day and it was found that, at first, before the reaction was carried to completion, the desulfurizing was not very great. In other words, samples from ladles to which no desulfurizing compound was added showed about the same sulfur content as the first samples of the iron taken from the ladles containing the desulfurizing compound. As the pouring progressed, the sulfur content went down in the cast-iron samples; toward the end of the day, however, the sulfur rose in the treated samples. According to the conclusions of the author, this happened because the slag was allowed to remain on top of the ladle, which by that time became saturated with sulfur, in consequence of which no further desulfurization could take place.

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C. A. MEISSNER.—We should be careful about stating at what sulfur limits the results mentioned in this paper really take place. In our practice, where we have a great many furnaces under very different conditions, where sulfur has run in the coke from, well say, about 0.65 to 0.70 per cent. and in some cases about 0.85 or 0.90 per cent., we do not find any of the deleterious results that are here stated to occur in those furnaces that have the higher sulfur coke.

I presume when the sulfur runs about 1 per cent., these figures will begin to show and show materially where they run more than 1 per cent. In the first place, there is always margin enough in our practice to overcome these differences, and we have the practical results in some of our very large plants where the coke consumption is about the same in both cases from month to month. The tonnage is about the same; in fact, just recently one of the large plants having about 0.90 or 0.95 per cent., sulfur coke has been running practically a record for a period of several months and the coke consumption has been fully as low, in fact, lower than some of the plants that had lower sulfur coke. In all calculations such as these, there are certain limitations that, particularly in a blast furnace, are covered by the necessary margin they carry.

In the case of the smaller furnaces, where the sulfur content of the coke is 1 per cent. and over, the figures here given are going to approximate actual results, and the coal and coke suppliers should make every possible effort to reduce the sulfur content by clean mining of the coal, or the proper cleaning of it before it is coked.

Chemical Equilibria During Solidification and Cooling of White Cast Iron

By H. A. Schwartz, M.E.* and (Mrs.) Anna Nicholson Hird,†
Cleveland, Ohio

(New York Meeting, February, 1925)

Of the outstanding investigators of the system iron-carbon-silicon Gontermann,[1] Charpy and Cornu-Thenard,[2] and Honda,[3] only the first touched on the chemical composition of the solid and liquid phases in equilibrium with one another. He concluded that his data did not permit a decision as to which of an indefinitely large number of pairs of compositions of liquid and solid would be found in any given case.

If through the three dimensional equilibrium diagram of the iron-carbon-silicon system an isothermal plane is passed in the region of partial solidification, two lines of intersection with the liquidus and solidus, respectively, are obtained, also a point marking the alloys' composition. If, in this plane, a straight line is drawn through the point, and intersecting both the liquidus and solidus isothermals, the two intersections mark a liquid and a solid alloy that may be chemically in equilibrium at the chosen temperature. From thermal data alone, Gontermann could not assign any particular direction to the line and, hence, could not determine which pair of conjugate points to choose.

A separation of the liquid and solid for analysis, obviously, presents grave experimental difficulties. During the solidification of white cast iron, austenite of progressively higher carbon will separate as the temperature falls and cementite will appear suddenly at the freezing point of the eutectic. This cementite will be accompanied by a corresponding amount of austenite which, for our purpose, will be chemically inseparable from the primary austenite. We have attempted to decide on the conditions at the end of the freezing by a chemical separation applied to the solid metal.

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[1] Iron-Silicon-Carbon Alloys. *Jnl.* Iron and Steel Inst. (1911) **83**, 421.

[2] Researches on the Iron, Silicon, and Carbon Alloys. *Jnl.* Iron and Steel Inst. (1915), **91**, 276.

[3] On the Structural Constitution of Iron-Carbon-Silicon Alloys. *Jnl.* Iron and Steel Inst. (1923), **107**, 545.

Experimental Procedure

The cementite of various samples of white cast iron was separated by the electrolytic solution of the austenite. The electrolyte consisted of a 10 per cent. solution of concentrated HCl in water, and was frequently changed in order to keep the concentration of $FeCl_2$ at a minimum. A potential of less than 4 volts was maintained between the hard iron anode and a platinum or copper cathode, resulting in a current density of not over 5 ma. per sq. cm. Too high an acid concentration, potential or current density will decompose the cementite.

As an exact quantitative separation of cementite was found impracticable, because of mechanical losses, an indirect method was adopted. The density of the original hard iron was determined by the Archimedean principle. A fragment of cementite of suitable size was weighed. The surface pores were filled with paraffin, avoiding as far as possible any external layer of measurable thickness, and the volume of the treated specimen was determined by the difference of its weight in water and air. From this volume and the original density of the metal, its weight before electrolysis, and from its final weight, the recovery of cementite may be calculated. The necessity for this indirect method is probably the major source of error in the accuracy of interpretation of the analytical data.

When applied to a moderately rapidly or slowly cooled specimen, this method removes the ferrite and leaves behind the eutectic, proeutectoid, eutectoid cementite. If, before the separation, the specimen is heated above A_1 and quenched, the last named will go into solution and the resulting austenite and martensite will dissolve in the subsequent electrolysis, leaving eutectic and proeutectoid cementite. It was hoped that by quenching from just under the solidus, the latter could be dissolved; but this was impracticable because of the rapid decomposition of Fe_3C at these temperatures. From the composition and recovery of cementite, the composition of the dissolved material can be calculated. In all, seventeen specimens of carbide were studied.

It seems unnecessary to burden this paper with all the data as the results point to a quite simple conclusion. Although the analytical work was probably correct to a degree of precision consistent with the best practice on iron and steel, the errors with respect to cementite recovery and the need of obtaining certain values by difference makes it quite likely that the calculated analyses contain quite noticeable errors. These do not, however, prevent usable conclusions as to the limits approached in the reactions.

Attention is called to the high silicon content of cementite, as compared with ferrite. The negative value of carbon in ferrite points to a cumulative error, but indicates that practically no cementite was dissolved. It is obvious that the manganese and sulfur in the cementite

exist substantially altogether as MnS. The small amount of sulfur apparently left in ferrite possibly is to be interpreted as representing MnS dissolved from the cementite by acid. Nearly all the phosphorus (93 per cent.) is found with the cementite.

TABLE 1.—*Composition of Original Metal, Total Cementite, and Ferrite*
(Average of three typical samples)

	Original Metal, Per Cent.	Total Cementite, Per Cent.	Ferrite by Difference, Per Cent.
Total	100.0	41.3	58.7
Carbon	2.63	6.44	−0.08
Silicon	0.87	1.58	0.36
Manganese	0.32	0.26	0.37
Sulfur	0.066	0.130	0.023
Phosphorus	0.151	0.341	0.021
Mn in excess of MnS	0.209	0.04	0.33

Table 2 indicates that none of the silicon of the cementite and much of its phosphorus is in the eutectoid portion, while the original manganese of the austenite distributes in equal concentration between ferrite and eutectoid cementite.

Table 3 shows that in the same casting, in a thin section (1/8 to 1/4 in. thick) the silico-cementite corresponds to 0.46 per cent. silicon in the hard iron, while in a thicker section (about 1 in. thick) it corresponds

TABLE 2.—*Distribution of Elements between Eutectoid and Eutectic and Proeutectoid Cementite*

	Eutectic and Proeutectoid Cementite, Per Cent.	Eutectoid Cementite, Per Cent.	Ferrite, Per Cent.
Silicon	1.75	0.00	0.08
Manganese	0.33	0.27	0.24
Sulfur	0.165	0.00	−0.018
Phosphorus	0.144	0.68	0.033
Mn in excess of MnS	0.05	0.27	0.24

to 0.77 per cent. Unfortunately, the original material was no longer available for analysis because of the loss of certain specimens. It is known, however, from its origin, that the metal was manufactured to have a silicon content of about 0.80 per cent.

TABLE 3.—*Effect of Freezing Rate on Distribution of Silicon between Austentite and Eutectic*

	Frozen Quickly, Per Cent.	Frozen Slowly, Per Cent.
Recovery of eutectic and proeutectoid cementite.....	37.0	31.0
Silicon content of eutectic and proeutectoid cementite..	1.28	2.48
Corresponding silicon content of original metal.....	0.46	0.77

CONCLUSIONS

We believe that the results here recorded as typical of our work warrant the conclusion that during the freezing of the ternary system iron-carbon-silicon, the silicon will be rejected to the liquid and will all be found in the eutectic cementite, if the cooling is slow enough to permit the attainment of equilibrium.

We are unable to say whether this silicon exists as silico-cementite or as a separate structure of silicide, interlacing with the cementite. Having sought in vain for evidence of the latter, we incline to the former explanation as the simpler.

Manganese, when present in amounts of the order of magnitude of 0.25 per cent., will freeze out with the austenite. Any MnS present will freeze out in the very beginning and will be rejected as a floating solid particle into the last freezing regions. It becomes trapped in the ledeburite as a microscopically discrete constituent.

Much of the phosphorus separates in a form that is inseparable, by our methods, from eutectoid cementite. It appears to have been equally soluble in the original cementite and austenite, but to have separated from the latter like, or in, the eutectoid cementite at A_1.

The original austenite contains all the non-sulfide manganese when present in small amounts; this manganese is equally soluble in ferrite and eutectoid cementite on passing through A_1.

DISCUSSION

N. B. PILLING,* Bayonne, N. J.—The last column of Table 1 gives the composition of ferrite, which is obtained largely by indirect methods. The ferrite contains approximately 0.4 per cent. silicon, whereas the original metal contains 0.9 per cent. In Table 2 the ferrite has much less silicon. What is the difference between the two ferrites? The paper shows that these iron-silicon-carbon alloys have two varieties of carbide,—one containing silicon and the other substantially silicon-free, the silicon-free carbide being present in the eutectoidal part. Is there physical, chemical, or any other difference between them; especially is

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there any difference in the rate of graphitization of the two carbides? In Table 2, the authors give no estimation of the carbon contents of these three constituents; did they examine the carbon content of the eutectoidal carbide which they report as being free from silicon to verify its identity as a carbide?

RALPH H. SWEETSER,* Columbus, Ohio.—Table 1 gives the carbon content of the original metal as 2.6 and 3 per cent.; the silicon and sulfur are fairly normal but the sulfur is a little bit high. But with 0.87 per cent. silicon, it seems that the total carbon is very small. I would like to know what kind of pig iron was used.

H. M. BOYLSTON,† Cleveland, Ohio.—Perhaps I can answer that question. They used cupola metal, which is then blown in a small bessemer converter and finished in an electric furnace, after adding more iron from the cupola.

ALBERT SAUVEUR,‡ Cambridge, Mass.—It will be a surprise to many of us, I think, to learn that so much of the impurities present in white cast iron, namely phosphorus, sulfur, silicon, and manganese, is present in the cementite and so little in the ferrite. The visualizing of the mechanism of the solidification of white cast iron may be, in this connection, of some interest. White cast iron, like many other metallic solid solutions, crystallizes through the formation of dendritic crystals, the axes of which consist of saturated austenite and the fillings of the eutectic cementite-saturated austenite. The impurities should segregate in the fillings, that is in the eutectic, while the austenite axes should be quite free from them. On further cooling, the saturated austenite of the axes transforms into proeutectoid cementite and pearlite; and because of the relative purity of the axes this proeutectoid cementite, as well as the eutectoid (pearlite) cementite and the eutectoid ferrite resulting from the transformation of the axes, should be quite free from impurities. The eutectic cementite of the fillings, on the contrary, should be more impure as well as the proeutectoid cementite and pearlite resulting from the transformation of the eutectic austenite. If these inferences are correct, we are led to conceive the presence in white cast iron of pure and impure cementite, the former resulting from the transformation of the pure austenitic axes of the dendrites, the latter from the more impure fillings; and for like reasons it should contain pure and impure ferrite. The demonstration of the accuracy of these conclusions by metallographical, chemical, or other means, should prove of considerable interest.

H. A. SCHWARTZ (author's reply to discussion).—The difference in silicon content of ferrite, alluded to by Mr. Filling, is, no doubt, explained

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by the fact that the two materials under investigation cooled at different rates. As pointed out in the paper, the slower the cooling rate, the more silicon appears to be rejected toward the last freezing ingredient; consequently, the more is found in the eutectic cementite—and the less in the ferrite derived from the decomposition of primary austenite.

It is known quite definitely, that the ferrite of low-silicon content was derived from a sample of larger cross-section than that of high-silicon content, hence that it probably cooled more slowly. The carbon contents were omitted from Table 2 because the carbon of the ferrite is determined only indirectly by the method indicated in the paper. The writer's present recollection is that, as a matter of fact, the carbon content of this particular ferrite came out somewhat negative.

Inasmuch as the method used is subject to the inherent errors pointed out in the paper, these several carbon contents were not introduced in the table, as we did not wish to lay any stress on whether or not the carbon was always exactly theoretical for cementite. As a matter of fact, the various varieties of cementite always came out a carbon content of the proper order of magnitude for that compound.

Through the kindness of the Union Carbon Research Laboratories, a sample of pure cementite and of silico-cementite were examined with the *x*-ray spectrometer; both showed the pattern characteristic of cementite, as described by Westgren. The silico-cementite showed other lines also, which Mr. Bain believes to be due to the presence of iron oxides. Opportunity was lacking, however, to follow up the matter in great detail, as might have proved quite interesting.

It is the writer's opinion that cementite, as such, does not graphitize, but that this reaction takes place only after the cementite has gone into solid solution The reasons for this viewpoint will be expounded elsewhere. If it be correct, then the composition of cementite should make less difference to graphitization than the composition of the solvent material. Definite information on this point can not be given.

Professor Boylston's reply to Mr. Sweetser is correct; we merely add that the chemical compositions, with respect to carbon, are such as may be used for various purposes in the manufacture of malleable castings. In general, the higher carbon metal here used is not that employed for the manufacture of commercial castings of the so-called "certified" grade. Most hard irons for such a purpose would run under 2.6 per cent. carbon and would be made either as indicated by Professor Boylston, or by remelting in the air furnace, mixtures of hard and malleable scrap, pig iron, and steel, calculated to give the desired results.

We are obliged to Professor Sauveur for his exposition of the mechanism by which variations in the purity of ferrite or cementite may be brought about by the process of selective freezing. It is hoped that the results we have recorded may serve as partial support for the viewpoint he has presented in his discussion.

Finishing Melting Temperatures of Simple Ingot Steels

BY HENRY D. HIBBARD, PLAINFIELD, N. J.

(New York Meeting, February, 1925)

THE finishing and casting temperature of steel is a subject concerning which there is so much to learn that some temerity is required to write about it. This paper is, therefore, suggestive rather than dogmatic, though the views expressed seem now to the writer to be correct; nevertheless, they may be modified by future developments or discoveries but until then may be of some utility, particularly to beginners in the making of steel. Consideration is limited to the temperatures of simple steels, also called carbon steels, which are those in which carbon is the only element introduced for the purpose of conferring desired physical properties. Alloy steels will receive attention later.

Three things largely determine what a batch of steel really will be; viz., composition, casting temperature, and rate of teeming. Each has its advocates as being the most important; but they are so interrelated that each must conform to or be right for the other two. When one is claimed to be the most essential to have right, that, probably, was the one that it was found had to be of a certain description, within narrow limits, to suit the already adopted variations of the other two; that is, it was the last of the three to be brought into line.

The term "casting temperature" is rather indefinite as there are several temperatures to which the term may be applied. Most writers who have mentioned casting temperature of steel have alluded to it in relative terms. The few who have given actual temperatures, including Langmuir, Burgess, Styri, and Bash, do not give full information about them. Their results demonstrate the efficiency of pyrometers used rather than aid the steelmaker. In order to understand and use the temperatures, one should know in each case what the steel was, the stage at which the temperature was taken, whether it was usual or not, and whether or not it was right for that steel at that stage. When these

particulars are not noted, it may be proper to assume that the steel was of some commercial description, with carbon say between 0.3 and 0.5 per cent., and was at about its usual and proper temperature. Such assumptions, however, are not wholly dependable.

Classification of Steels

For the proper consideration of casting temperatures, all steels should be divided into three classes: killed steels, which settle in freezing and contain no gas holes; partly killed steels, which contain some gas holes that are more or less harmful; and effervescing steels, which evolve gas freely in the molds. Steels of these classes behave differently from each other, with variations of casting temperature.

Pouring Temperatures

It is well known that for pouring any given ingot of a given steel there is a proper, best, and ideal temperature for the metal. A second temperature at which serviceable steels of certain of the harder grades may be cast will be referred to later. Too great, yet moderate, deviation from either of these temperatures, above or below, will lead to some degradation in the quality of the product.

Though the fact will be admitted, the reasons why an "off" temperature is harmful are not fully known. It is difficult to see how a variation in temperature can affect the quality of the metal *per se* and probably such a variation does its work more on the non-ferrous ingredients (solid, liquid and gaseous) than on the metal itself.

The effect of temperature on crystallization, and particularly on the formation of "chill" dendrites in the outer metal, is most important. The hotter the steel as it enters the mold, the longer time these dendrites will be in forming, the larger they will be and the more completely the freezing metal in forming them will reject the non-ferrous substances it contains, both solubles and insolubles, causing them to collect along the grain boundaries where they form relatively weak interfacial layers. The non-ferrous soluble substances include carbon, sulfur, phosphorus, and oxygen, combined with iron as carbide, sulfide, phosphide, and ferrous oxide, all but the carbide being harmful. The insolubles are chiefly oxides of iron, manganese, and silicon, more or less completely combined as silicates, and sulfide of manganese; they are all harmful.

This concentration of the impurities along the crystal or grain boundaries is quite enough to account for inferior quality and to cause the steel to crack in hot-working. The more the impurities the greater is the damage from too high temperature, and vice versa as will be considered later. Carbon in carbide of iron so segregated may be redistributed through the mass of the metal by continued suitable heating, also,

possibly, phosphorus to some extent; the insolubles may not be but may remain as permanent defects.

It is claimed, and is probably true, that casting too hot increases segregation. When well-made steel is killed, as by the addition of 0.25 per cent. of silicon or more, and cast at the ideal temperature into 3-ton ingots, there is little if any segregation.

The actual temperatures at which the different steels melt and those they should have in the furnace and at the different stages, until they are in the molds, are practically unknown but one can make assumptions that may be of some value. The fusion points of iron (1530° C.) and of iron with varying contents of carbon are given. Therefore we know the effect on fusibility of a given amount of carbon but not of manganese and silicon, the chief other ingredients of simple steels. We may, however, fairly assume their effects in that respect to be about proportional to their percentages. Manganese melts at 1230° C., or 300° below iron, and silicon at 1420° C., or 110° below. So the effects of 1 per cent. of each in iron on its melting point may be tabulated as follows:

1 per cent. of carbon lowers melting point 90°
1 per cent. of manganese lowers melting point 3°
1 per cent. of silicon lowers melting point 1.1°

The effects of manganese and silicon in simple steels are thus shown to be practically negligible. They are probably alloyed with the iron while carbon, which has great influence, is undoubtedly in combination.

The melting point, and therefore the tapping temperature, both become lower with increase of carbon in the steel. The ideal tapping temperature is sufficiently above the melting point to allow for the loss of heat in tapping, transferring, and teeming. The amount of excess heat required varies with the kind of steel, size of charge, time between tapping and completion of teeming, and other minor conditions but is quickly learned for any particular situation. The low-carbon steels, being hotter, cool more rapidly than those with higher carbon and therefore require a correspondingly greater heat margin than the latter.

Table 1 has been compiled as an attempt to give the proper temperatures for finishing and casting simple steels of different carbon contents. All the known published temperatures (mostly conflicting and some manifestly incorrect) as well as Caspersson's table have been considered and utilized and, omitting units, the figures given are thought to be near actual American practice. Four temperatures for each steel are given; viz., that of the metal in the furnace just before tapping, that of the stream of steel flowing from the furnace spout into the ladle, that of the stream entering the mold at the beginning of teeming, and that of the stream at the end of teeming. Either of the first three mentioned might with some justification be called the casting temperature. The proper

finishing temperatures of open-hearth and bessemer steels of the same composition are thought to be nearly alike. The table is, of course, subject to modifications as facts become known.

TABLE 1.—*Assumed Finishing Temperatures of Open-hearth Simple Steels*

50-ton charge, 3-ton ingots; steel finished in furnace; American practice

Carbon, Per Cent.	Melting Point, Degrees C.	Ideal Temperatures			
		In Furnace Just before Tapping, Degrees C.	Tapping Entering Ladle, Degrees C.	Teeming	
				Beginning, Degrees C.	End, Degrees C.
Pure iron	1,530				
0.10	1,520	1,620	1,615	1,580	1,550
0.20	1,511	1,610	1,605	1,570	1,540
0.30	1,501	1,600	1,595	1,560	1,530
0.40	1,492	1,590	1,585	1,550	1,520
0.50	1,483	1,580	1,575	1,540	1,510
0.60	1,474	1,570	1,565	1,530	1,500
0.70	1,465	1,560	1,555	1,520	1,490
0.80	1,456	1,550	1,545	1,510	1,480
0.90	1,447	1,540	1,535	1,500	1,470
1.00	1,438	1,530	1,525	1,490	1,460
1.10	1,429	1,520	1,515	1,480	1,450
1.20	1,420	1,510	1,505	1,470	1,440
1.30	1,411	1,500	1,495	1,460	1,430
1.40	1,402	1,490	1,485	1,450	1,420
1.50	1,393	1,480	1,475	1,440	1,410

Table 1 contemplates that the steel is to be finished in the furnace. When, however, ferromanganese and, it may be, other alloys are added cold to steel in the ladle the temperature of the unfinished steel in the furnace should be higher on an average by about 15° (varying of course with the quantity of alloys so added), to provide heat for melting them.

The table further contemplates no unnecessary delay between tapping and the beginning of teeming, the interval being assumed to be about 6 min. When the metal is intentionally held in the ladle, as when time is afforded to allow the sonims to escape, and that period is extended to 20 min., the temperatures of the steel in the furnace and entering the ladle should be higher by about 20°.

It is assumed, in the table, that the charge weighs 50 tons and is top-cast into 3-ton ingots; teeming is assumed to take 30 min. When the time consumed in teeming varies, the tapping temperature should vary also to compensate therefor; thus a larger charge or smaller, and therefore a greater number of, molds will call for hotter steel, and *vice versa*.

The fall in temperature of 30° during teeming allows a deviation of 15° from the ideal mean, which probably should not be exceeded. This fall is somewhat less than that indicated by recently published pyrometric determinations but has been adopted tentatively for several reasons. Caspersson's table and experiences at Fagersta and Steelton indicate that a variation of 10° makes steel somewhat "off" in ingot structure and quality. In addition, the first metal to flow from the tap hole is that at the bottom of the bath and, therefore, the coldest of the charge. The hotter metal which follows is well mixed with that already in the ladle as long as the stream is large, so that when the slag comes, the metal in the ladle is of practically uniform temperature; but the ladle lining will be hotter at the bottom than at the top, having been submerged longer by the molten metal. The slag, which comes last from the furnace, is hotter than the metal and, when of proper consistency, quickly chills on top, forming a slowly conducting hot blanket over the metal. For some time after all the charge is in the ladle, the steel gives up heat to the ladle lining faster than it does to the top covering of slag. In the ladle the colder metal tends to settle at the bottom, so that it will be the first to leave the ladle when teeming, the hotter staying at the top and being consequently the last to be teemed. The metal last to leave the ladle must be losing heat very slowly because of the hot ladle lining and slag blanket. So when the ladle has an amply thick lining and is heated red hot inside before the steel enters, and conditions are normal, there may be little difference in temperature between the first and last steel to be teemed.

Relatively hot steel calls for a small nozzle, which requires proportionately longer time in teeming and, possibly, a wider range of temperature during that operation; therefore steel may be too hot at the beginning or too cool at the end for the best results. With high-quality killed steel, this may not be important, as referred to later; but for ordinary steel, it may be an argument in favor of a low casting temperature and larger nozzle.

The use of a pyrometer in the shop to tell the temperature of the open-hearth bath metal, to the writer seems to be of doubtful merit. It is not needed as knowledge of actual temperatures, in degrees, is not essential for obtaining regularly good, or even the best, results. Good judgment, based on the points mentioned below, and ample experience are enough. Still it would be well to know what those temperatures are as an aid to complete understanding of the art and for explaining discrepancies, and particularly for comparing one practice with another.

When melting steel, the furnaceman becomes familiar with the brightness of the light from his furnace, as seen through his blue glasses, and with the relative brightness of the flame, the cooler back wall, the still cooler surface of the slag, and the yet cooler wakes of the gas bubbles

rising through the slag from the metal. Then he learns much when taking furnace tests and samples. The way in which a stirring rod is melted off and the time required therefor, the appearance and behavior of the metal in the test cup, the length of time it remains molten, the skull remaining in the cup, if any, and the speed of solidification in the test mold, all indicate the temperature of the metal. Or he may slowly pour out a cupful of metal in a stream about the size of a lead pencil when the skull remaining, if any, enables him to judge his heat. The vigor of the boil (bearing in mind the carbon content of the metal), the behavior of the metal in the test cup and ingot, and the basicity of the slag give him information as to the tenor of oxygen in the metal, which element tends to lessen the fluidity at any given temperature, particularly of low-carbon metal. With all these guides, his probable error is perhaps less than that involved in taking the temperature of the surface of the bath with a pyrometer, then estimating the emissivity of the slag and judging the difference in temperature between the top of the slag and the unfinished steel beneath. The things noted, which are perhaps the most important of those that enable the relative temperature of the metal to be ascertained, are done before it is too late to correct the temperature, if wrong. Determination of the temperature of steel running into the ladle or mold is chiefly of value in helping to get future heats right in that respect, though too hot a heat may be held a little extra time in the ladle, at some risk, before teeming is begun.

In any steel that has had proper treatment, in other respects, in the furnace, the usual defects from casting at too low a temperature are from misrunning and cold shuts. Certain steels, however, covering the whole range of carbon contents, referred to by Caspersson, Brinell and others in Europe, which were cast too cold, were claimed for that reason to be badly infested with gas holes. Those holes were located at random throughout the ingot, as though made by gases that separated when the steel was in the mushy stage just before actual solidification, a condition that seems to have existed throughout the whole ingot at about the same time, due to the low temperature. Steel cast too hot has other defects, which are noted hereinafter.

In common American practice, the proper or ideal casting temperature for any ingot steel is, generally speaking, the lowest that will admit the whole charge to be successfully poured without an important amount of solid metal (skull) being left in the ladle.

Caspersson's table, published in 1882, gives diagrammatically the structure of bessemer steel ingots of different carbon contents blown and, presumably, cast at different temperatures. It is still of great interest. It shows that for soft steels, containing under 0.40 per cent. of carbon, and, from the ingot structure given, presumably effervescing, there is one ideal temperature (as in American practice), while for harder

steels, having 0.4 per cent. or more of carbon up to 1.52 per cent., there are two temperatures at which good ingots may be made. At the higher of these two temperatures solid piping ingots are obtained, while at the lower the ingots are thick skinned; that is, are sound in their outer parts but have some deep-seated or central gas holes. If cast at a temperature midway between these, the ingot will have ruinous skin holes. The higher the carbon, the lower the temperature that will give the kind of ingot required, whether solid piping or thick skinned. The temperatures are, of course, merely comparative, the actual temperatures not then being known; but by assuming the hottest, which is too hot for steel containing 0.04 per cent. carbon, to be 1650° C. and the coldest, which is too cold for steel having 1.52 per cent., to be 1400° C., and interpolating those between, a reasonable list of 30 temperatures is obtained. These, it must be admitted do not agree exactly with Table 1, perhaps either because the assumptions made are not strictly true or because his 29 intervals are not uniform, as they are of necessity when obtained by interpolation. It corresponds most nearly with the mean of the teeming temperatures given and, indeed, it is likely that Caspersson based his table largely on observations of steel in the molds.

To give an example, Caspersson's steel with 0.55 per cent. carbon is sound and settling at the upper limit, and sound except for the gas holes in and near the center at about 1530° C. (by interpolation), while at about 1590° and about 25° each way the steel is ruined by skin holes. Another notable point is that each temperature near the middle of the range is right for two different steels. Thus 1545° (always assumed), which is too cold for steel having 0.15 per cent. carbon, is right for thick-skinned ingots containing 0.45 per cent., wrong for steel with 0.95 per cent., and right for piping steel with 1.41 per cent.

Caspersson's heats were blown from crude iron containing from 3 to 5 per cent. of manganese and no recarburizer was added. No one whom I have asked has been able to give me details of Caspersson's practice, but Brinell and Akerman vouch for the genuineness and reliability of Caspersson's work.[1] Particularly I have wanted to know how he made thick-skinned ingots containing from 0.40 to 1.50 per cent. carbon. None of the ingredients of his steels, except carbon, are given, which adds to the difficulty of explaining or understanding his results. His only solidifier, if he added any, must have been silicon, as aluminum and titanium had not then been made in sufficient quantity for such use.

No practice in America, known to the writer, corresponds to that of Caspersson either in respect to two casting temperatures for medium and high-carbon steels or for ingots of such steels having sound exteriors and central gas holes. Campbell did say that occasional excessively hot

[1] Richard Akerman: The Bessemer Process as Conducted in Sweden. *Trans.* **22**, 265.

bessemer heats at Steelton were of good quality and they may have corresponded with Caspersson's higher temperature for settling steel, but the practice was not regular or intentional.

At Fagersta, Sweden, in 1916, they were making most excellent acid open-hearth steel for the tension members of flying machines. The furnaces were of 20 tons capacity and the ingots were 10 by 10 in. top-cast, large end up, with hot tops to limit the pipe. The tops were so made as to be broken off cold to show if the pipe had penetrated the body of the ingot or not. The steel rolled beautifully, like wax, in the blooming mill, without a crack. I was told that they had open-hearth steel melters who could bring their heats out regularly within 10° C. of the proper temperature. At the time the claim seemed to be unwarranted but not so now. A skilful melter can make practically uniform steel, provided his conditions of plant, fuel, and materials are not changed, while Caspersson's table shows that a variation of 10° from the ideal finishing temperature may make steel somewhat "off" in quality. Campbell thought that a variation of 10° C. was noticeable in bessemer steel, that is, a change in the amount of scrap added to cool the charge which would cause a change in temperature of that amount was clearly recognizable.

Killed Steel

In killed steel, the ill effect, if any, of a too high casting heat is pronounced ingotism, manifested through the behavior of the carbide of iron as well as the solid and liquid impurities, and particularly their concentration along the grain boundaries as described. With impurities at a minimum, defects attributable to them are proportionately slight. There is evidence which indicates that a steel containing considerable carbon, say over 0.4 per cent., which is well purified of excesses of oxides and gases and then killed by the addition of gas solvents, particularly silicon, is, chiefly because of its freedom from sonims, practically but little injured in quality by being cast at a temperature considerably higher than would be ideal in American practice for open-hearth steels of similar composition. There is, on the contrary, the advantage that the higher temperature, by affording longer time during which the steel remains fluid, allows any sonims present to separate more completely, giving cleaner and, therefore, better steel. It may, however, crack in hot-working because of its "chill" dendrites.

Crucible steel, well killed, may be cast exceedingly hot without damage to its quality; even so hot as to melt a groove in the cast-iron mold if the stream of steel in teeming plays against it for a second or two.

Brinell, in Sweden, 25 years ago considered that the casting temperature of steel was of secondary importance to composition. His experience was, presumably, similar to that of Caspersson with killed acid

steels having generally over 0.4 per cent. carbon made from a highly manganiferous charge, with, possibly, addition of silicon at the end of the heat. As already noted, steel so made may perhaps not be injured much, if any, by a too high casting temperature, or perhaps at Caspersson's upper correct temperature for the harder steels.

The reports we have of open-hearth steel cast excessively hot (from an American point of view) are from Europe, and pertain to high-quality killed steel, such as for ordnance; where the greatest care is demanded to rid as completely as practicable the unfinished steel before tapping of all ingredients that are hurtful to quality, particularly oxides and silicates. In England, France, and Italy, it has been reported, steel for cannon is cast exceedingly hot. That may be right for their steels, presumably acid, which are said to be well purified of all oxides in the furnace by the action of carbon and manganese, ample time being allowed. Giolitti says that such steel, made in Italy, is likely to be cracked in the skin in forging even when it is carefully done, which is a sort of guarantee that it will pass inspection, particularly in meeting the physical tests. The cracking is thought to be due to excessive development of the dendritic "chill" crystals with attendant concentration of carbide between them. A desideratum in American practice for killed steels is that the outside of the ingot shall be sound and not crack in forging or other hot-working.

Certain European steelmakers have claimed that the rate of teeming is more important than temperature on the quality of fine steels (presumably of the harder grades) particularly in favoring freedom from cracks when hot-worked. They consider slow teeming essential, to insure which small nozzles, down to ¾ in. in diameter, requiring 1½ to 2 min. to the ton of steel top cast, or large bottom-cast groups are employed. These measures seem to be called for because of the avowedly high temperatures at which their steels are tapped. They do not tell enough about their methods to enable an average American to understand their practice. While the whole story cannot be told, to get a reasonable conception of the practice, one should know the size of the furnace and molds and the state of the unfinished steel in the furnace as to temperature, boil, and residual percentages of carbon, manganese, and silicon; if basic, one should also know the contents of iron and silica in the slag. In addition, full information as to the additions, manner of making them, time elapsed after their addition before tapping, and the final composition and temperature of the steel entering the mold should be had.

Partly Killed Steels

The ill effects of a too high casting temperature on partly killed steels may arise from the action of the high heat on one or more of the solid, liquid, or gaseous impurities contained. Such steels, as a rule, are not well made, but they vary much in that respect. In the mold,

some rise, some stand, and some settle; the best-made settle nearly as much as if wholly killed. Usually, they also contain unduly great quantities of oxides, both solid and liquid, which become sonims in part at least.

When the steel is cast too hot, marked ingotism is present. Many of the sonims, which are too small to escape by floating to the top, are collected between the chill dendrites. The dendrites are larger than they would be if the steel were cast at the ideal temperature. The central portion of the ingot may, however, be cleaner of sonims because of the excessively hot, and therefore longer fluid, metal as in the case of killed steel. Such steel so cast is ordinarily somewhat red short and prone to crack when hot-worked.

Because of the many varieties of partly killed steels, statements about them, or any of them, must, to be intelligible, be specific and tell the kind of steel under consideration.

Effervescing Steel

When making effervescing steel, the casting temperature, through its effect on the gases, is the condition that determines the quality and hence the usefulness of the product. It affects (1) in part the activity of the boil of the bath in the furnace, which, however, depends also on the supply of oxygen that reaches the metal, and (2) the rate of effervescence in the molds. The great thing demanded in this steel is that the ingot shall not contain skin holes. None whatever can be allowed in steel to be rolled direct from ingot to finished plate, but a few small ones may be obliterated by a second heating and rolling when that method is followed. With a proper boil, the gas that forms the skin holes (probably hydrogen) will be present in the metal only in a permissible minimum. Then with adequate effervescence (which, with correct casting temperature will be obtained) no harmful skin holes will exist in the ingot. The hotter the steel is above the ideal temperature, the weaker will be the effervescence in the mold.

Effervescence is the escape of the gases, chiefly carbon monoxide, in myriads of bubbles from the molten steel in the mold, the uprush of which keeps the metal in violent motion with a churning effect, while it progressively freezes from the outside toward the center. The rising bubbles throw up a small brilliant shower of sparks from the molten metal, which gradually diminishes as the metal freezes Steel containing as high as 0.4 per cent. carbon may be made by this method, but the action is better or more easily brought about with lower carbon, say below 0.20 per cent.

Just why a certain vigor of boil is necessary is not definitely known, but probably when it is right, considerable of the dissolved hydrogen and nitrogen is carried off by the escaping myriads of carbon monoxide

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bubbles, so that the steel in the ladle and molds contains substantially less of them than when the boil is too gentle. The higher the temperature the greater is the solvent power of the metal for gases; hence the quieter boil and the more plentiful is the supply of hydrogen to form skin holes. Thus the boil determines the saturation point of the metal for skin-hole gas, which fixes the distance in from the surface at which that gas begins to separate. It should be not less than ½ inch.

In an extreme case, when the boil is far too weak, the saturation point of the molten steel for hydrogen is passed almost at once, when it begins to freeze in the mold and bubbles of the gas separate from the metal and tend to cling to the solidified skin. With adequate churning, due to effervescence, practically all of these bubbles, except at the bottom of the ingot, may be dislodged, when they will rise to the top; but if the action in the mold is too gentle, some of them may remain and grow and so form skin holes. If there is no effervescence, the skin holes will cover the whole ingot.

Effects on Steel of Variations in Casting Temperatures

Let us consider the effects of variations in casting temperatures on steels containing 0.15 per cent. carbon. The steel is top-cast into 3-ton ingots and the temperatures are taken as at the beginning of teeming. The first case is when the boil and temperature (1575° C.) are right. The quantity of hydrogen in the molten steel may then be so small that the saturation point of the metal for that gas will not be passed until perhaps ½ in. of metal, or even more, has frozen on the outside against the mold walls. Then the hydrogen begins to separate as small bubbles that tend to attach themselves to the frozen shell of the ingot only to be dislodged by the churning effect due to the effervescence. A few of the hydrogen bubbles may remain on the sides, near the bottom, where the effect of the rising bubbles is naturally weak, for the reason that they begin to form there, and therefore are small. Skin holes will also occur in a zone extending over the bottom, the same distance in as on the sides, there being no washing effect in that zone. The frozen shell of the ingot appears at the top as a rim next to the mold, which rim grows inward and level as solidification progresses. A cast-iron cover plate is usually laid on when the rim is an inch thick or so (without which the metal in the center, which is the last to freeze, might rise a little), and the ingot when solid has a flat top, the metal neither rising nor settling. Such an ingot will have a solid skin of metal 2 or 3 in. thick, then a zone of intermediate gas holes, and inside of them, perhaps, a few central holes. It will be of good quality.

With slightly hotter steel (perhaps 1590° C.) the effervescence, while brisk, is inadequate and the metal rises in the mold a little so that the

rim rises toward the center, forming a frustum of a pyramid on which a cover plate is laid. Such steel will probably roll well and be free from pits in the plates and seams in the blooms made from it.

With still hotter steel (say 1610° C.) the steel may rise for an inch or two before it begins to rim in. The rim will then form a frustum. Such steel will be rather "thin skinned" and the metal covering the skin holes may be burnt through in the heating furnace and lined with oxide of iron, thus forming pits and seams in the rolled product.

When the steel is excessively hot (say 1630° C.), in the mold it has an oily appearance and continues to rise without stopping when teeming is finished, whether bottom or top-cast. There is no evolution of gas from the metal, at first, but after some minutes a little may break through the top surface and escape giving the ingot a ragged top. Such an ingot may increase in bulk 12 or 15 per cent. after teeming and will have a profusion of skin holes all over. When it is broken or cut in two the elongated skin holes are displayed on the exposed surface extending in 1 or 2 in. and close together like cells in a honeycomb. It is strictly correct to call such an ingot honeycombed. When rolled, these skin holes form ruinous defects, such as pits and scabs on the surface of plates and seams and tears in blooms.

If the boil is right but the bath is moderately too hot, the skin holes will be in some depth from the surface but deeper in there will also be a zone of intermediate holes.

Why low-carbon steel intended to effervesce will not do so when excessively hot is not known. A plausible explanation is that at the too high temperature manganese has power to decompose carbon monoxide, which would cause the effervescence, if present in normal quantity. This gas does not appear though other gases, presumably hydrogen and nitrogen, do, so it must be destroyed as it is insoluble in solid steel and if present in the metal would be expelled therefrom in freezing. Manganese is the only element present in quantity so it would seem that that element, under the influence of the high temperatures, is the cause. Though the volume of carbon monoxide in full effervescing steel is large, its weight is small and the quantity of manganese present is overwhelming. This power of manganese, if it obtains, is acquired within a rather small range of temperature, presumably 25° or 30°, but not at one particular degree as the effect is gradual. In high-carbon steels, the temperature of assumed decomposition of carbon monoxide by manganese, say over 1590° C., may not be reached because of the relatively low melting points, and hence of casting temperatures of such steels, but if it is attained no harm from that circumstance would result because all gases are, or should be, suppressed in such steels. This explanation is at variance with what might be expected from the calorific powers of carbon and manganese when combined with oxygen, but the effect of high tem-

perature in changing chemical affinities is but little known. Silicon, having a lower calorific power than carbon, decomposes carbon monoxide at a red heat so it is not impossible, or even improbable, that manganese, even though its calorific power is much lower than that of silicon, may do so at a sufficiently high temperature. The small amount of carbon present may permit of this when a larger percentage would not. It is only when making low-carbon steels that such a temperature is likely to be reached.

DISCUSSION

ALBERT SAUVEUR,* Cambridge, Mass.—This paper once more calls our attention to a question that has been much discussed by metallurgists but has never been answered in a satisfactory manner. Is there for each steel an ideal teeming temperature and if so what is that temperature, and what are the objections to teeming at a higher or at a lower temperature?

It is generally held that there is a teeming temperature, for each percentage of carbon in simple ingot steel, that will yield the best results and that that temperature is as little above the melting temperature of the steel as is consistent with the absence of cold shuts and of heavy ladle sculls. Higher teeming temperatures are generally considered injurious. The author, however, admits that good results have at times been obtained from steel teemed excessively hot.

The ideal ingot should have as fine a dendritic structure as can be imparted to it and should be as free as possible from what the author calls "chill dendrites." For a given composition these conditions depend principally on the rate of solidification, a slow solidification resulting in large dendrites and in pronounced chill dendrites. The rate of solidification in turn is affected by: (1) the size and form of the casting; (2) the character of the mold and its temperature at the time solidification begins, and (3) the teeming temperature.

It is generally stated that a high teeming temperature promotes a slow solidification and, therefore, a coarse dendritic structure and pronounced chill dendrites. It is well to point out that a high teeming temperature *per se* has no such influence—its retarding action on solidification is due to the fact that a hot metal heats the walls of the molds to a higher temperature and this in turn slows down solidification. Could this higher preheating of the molds be eliminated, there is no ground whatever for believing that a higher teeming temperature would cause coarser dendrites. Neither is there any ground for believing that the existence of chill dendrites has a detrimental action on the quality of the steel; they are objectionable, however, because they may lead to the cracking of the ingots in forging. A higher teeming temperature affords more time for

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the inclusions to leave the metal and, in well-killed steel, the evidences are not conclusive that a high teeming temperature is injurious.

HAAKON STYRI,* Philadelphia, Pa.—In the second paragraph, the author states that three things largely determine what a batch of steel will be—composition, casting temperature, and rate of teeming. He forgets the time for refining or finishing of steel in the furnace. He classifies steel as killed, partly killed, and effervescing, and seems to consider all these steels permissible. I may draw a parallel to this classification and say that steels are well made, poorly made, and rotten; and I do not mean that all killed steels are good. I do not think any steel containing blowholes is permissible at the present stage of metallurgy. It might have been permissible when steel making on a large scale was in its infancy, say thirty or forty years ago. Maybe one reason was that they could not get a high enough temperature to refine the steel properly and in order to get some kind of useful steel they had to adjust the temperature more or less to the ingot molds, sizes, sections, etc., in an endeavor to get the blowholes at the place where they did the least harm. But they always do harm. The steel is not good as long as it contains blowholes; all plain steel should be made without blowholes.

The author states that the skin holes found in ingots probably contain more hydrogen; I have not been able to find any reliable reference, or investigation, that shows that the blowholes themselves contain hydrogen. He also states that by adding certain elements he can prevent the formation of gas; for instance, by adding aluminum and silicon he can prevent gas evolution because these elements take up hydrogen and nitrogen. This seems to be impossible; we do not know, for metals like aluminum or silicon, what the solubility of gases are at the high temperatures. It is not possible to have hydrides or nitrides of these elements at those high temperatures, and the only possibility of having such metals absorb a large amount of hydrogen or nitrogen would be if they could form stable hydrides or nitrides. The whole explanation of the presence of blowholes seems to be the unfinished condition of the steel, that the oxygen is not reduced sufficiently.

The author says that the possible explanation of why low-carbon steels do not effervesce though excessively hot, is the presence of manganese, which should decompose the carbon monoxide. I have shown, in some previous papers, that the reducing power of carbon increases with temperature. In other words, at a higher temperature the carbon should reduce the manganese oxide and carbon monoxide would escape from the liquid steel. If there was a reduction of carbon monoxide by test both the oxygen and carbon must stay in the steel as manganese oxide and carbide.

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* Chief of SKF Research Laboratory.

George V. Luerssen,* Reading, Pa.—The optical pyrometer, up to the present time, has been considered more or less of a curiosity. The literature has been confined to occasional temperatures taken in the course of experimental work, much of which has had to do rather with the study of the adaptability of the instrument to various purposes than with its application to problems of control in practical melting operations. The author has been the first to take the mass of information thus accumulated and mold it into useful form. With Table 1 as a start, the time does not seem far distant when the practice of recording temperature observations on each heat of steel will be regarded as much a part of the routine of steel making as is the regular chemical analysis.

The temperatures shown in Table 1 are applicable to 50-ton open-hearth furnaces. It is interesting to compare these desired temperatures with data of a similar nature compiled over a long period on 6-ton electric furnaces. Before making such comparisons, however, it might be well to explain the method used in deriving these desired temperatures.

It has been found convenient, in the determination of proper tapping temperature of any steel, to use as a datum line the "skull temperature" of that particular analysis. By "skull temperature" is meant the lowest temperature at which the steel will flow from the ladle, and may be determined as follows: Temperatures are observed at intervals throughout the course of teeming, and these readings are plotted in a curve with temperature as ordinate and time as abscissa. On the colder heats, the curve falls to a certain definite point in temperature, after which it becomes horizontal, the temperature remaining constant down to the last metal. Ladles from heats showing this type of curve are invariably skulled, so that undoubtedly the last metal in such cases is of the lowest temperature at which it is possible to pour. This temperature has been called the skull temperature and, over a great many heats of various carbon contents, has been found to be about 10° C. above the iron-carbon liquidus. Having determined the skull temperature of any steel and knowing the drop in temperature during tapping, drop in temperature per minute during the time in the ladle, and duration of teeming, it is possible to estimate the desired tapping temperature.

The following list of skull temperatures for carbon steel has been determined. This list has been compiled from results obtained over a run of several thousand heats, all of which were teemed into approximately 10-in. ingots:

Carbon, Per Cent.	Skull Temperature, Degrees, C.	Carbon, Per Cent.	Skull Temperature, Degrees, C.
0.40	1492	0.90	1454
0.50	1484	1.00	1447
0.60	1476	1.10	1439
0.70	1469	1.20	1431
0.80	1461		

* Metallurgical Dept., Carpenter Steel Co.

Comparing this list with Table 1 will show that the skull temperatures are somewhat lower than the desired end temperatures; they range from 28° lower for the 0.40 per cent. carbon steel to 9° lower for the 1.20 per cent. carbon steel. Also, the desired tapping temperatures necessary to finish pouring 10° to 15° C. above the skull temperature on a 6-ton heat are about 15° higher than the tapping temperatures in Table 1. These results thus afford an interesting confirmation of the author's table.

It has been noticed on a number of heats of steel not properly finished, that the skull temperature is 10° to 15° higher than it is on properly finished heats of the same analysis; this is an interesting confirmation of the view that the presence of oxides tends to raise the freezing point.

A. G. Zimermann,* Washington, D. C.—The statement is made that 1 per cent. of manganese lowers the melting point of the mixture 3°, 1 per cent. of carbon lowers the melting point 90°, and 1 per cent. of silicon lowers the melting point 1.1°; these values apparently have been deduced by simply taking a direct proportion of the difference in melting points in iron, manganese, and silicon. If our experience with low-melting-point alloys and with the equilibrium diagram in general be followed, it would tend to justify the statement that the effect of one metal on another does not follow the exact ratio of the proportions of the two elements.

A. L. Feild,† New York, N. Y.—It should be possible from the published diagrams of the Fe-Mn and the Fe-Si systems to obtain a more accurate estimate of the effects of manganese and silicon on melting point than that given in the paper. The location of both liquidus and solidus curves have been determined for the former system by Guertler and Tammann (1907). Similar data relative to the Fe-Si system have been obtained by Levin and Tammann (1905). In addition, the ternary system Fe-Si-C has been investigated in part by Gontermann (1911). The effect of silicon, in particular, on melting point is much greater than would be predicted from a straight-line relationship, because of the occurrence of a eutectic between iron and the compound FeSi.

The statement that nitrides are dissociated at high temperatures is subject to at least two notable exceptions. The nitrides of both titanium and zirconium are known to occur in steel in a thermally stable and insoluble form. In the case of zirconium at least, the insoluble nitride may be largely eliminated from the molten steel with a resultant decrease in total nitride nitrogen content. Nitrogen is known to be appreciaby soluble in steel, and in those cases where the addition of an element, such as silicon, which does not form an insoluble nitride, prevents evolu-

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† Research Metallurgist, Union Carbide & Carbon Research Laboratories, Inc.

tion of nitrogen during solidification, the presence of the element probably increases the solubility of nitrogen in liquid steel.

George A. Orrok, New York, N. Y.—The author says that he would rather trust a trained eye than a pyrometer. By shielding the pyrometer, it is possible to get a temperature reading that will note the correct temperature reading and that can be used for the handling of the temperatures in the open-hearth furnace. Very good results can be obtained when such an instrument is installed and watched in connection with other indicating instruments than can be used in the open hearth. Whether they will ever reach the stage where they may be substituted for the trained eye is debatable.

George V. Luerssen.—Those who have had considerable experience with pyrometers will agree with the author that, at present, temperatures taken in the furnace are next to worthless and, if anything, misleading. It is a bad thing, in any case, to take initiative away from another. In other words, if you attempt to take temperatures in the furnace and control those temperatures you take a certain amount of initiative away from the workman; the reactions occurring in the furnace are so closely tied up with temperature and as he is accustomed to judging temperatures in other conditions by the eye, that giving a man actual temperatures is a hindrance rather than a help. As far as keeping control of temperatures is concerned, it has been found perfectly practicable to record heats, tapping temperatures, and pouring temperatures on curves; that is, making curves of each heat content and showing exactly the progress of these heats in teeming, so that the man can gage his eye for future heats. That plan has been worked out and has been found very satisfactory.

Albert Sauveur.—If you want to keep a knowledge of temperature away from the workman for fear of taking away his initiative you might also avoid telling him anything about the chemical composition for like reasons.

George V. Luerssen.—I did not mean to infer that a knowledge of temperatures should be kept from the workman. In the work thus far conducted, the men have been trained to think in degrees rather than in such indefinite terms as "hot," "cold," "hot-side," etc., and this has been accomplished by giving them a record of each heat tapped. In the absence of a definite and reliable method of indicating furnace temperatures, this appears to be the most satisfactory method thus far devised.

Those who have had considerable experience with the optical pyrometer will agree that at the present stage of our knowledge, temperatures taken in the furnace are next to worthless, if not actually misleading. Even though it were possible to obtain reliable temperature readings in the furnace, it is a question whether taking the iniative from the melter

in this matter of temperature judgment, which is so closely related to other conditions in the furnace, would not result in a hindrance rather than a help. On the other hand, it has been found practicable to control temperatures within very narrow limits by means of graphs showing the temperature history of the heat from tap to finish. These graphs, given the melter directly after the completion of pouring each heat, are a valuable aid in gaging the temperature of future melts. This method has been employed with entire satisfaction.

R. F. Harrington,* Boston, Mass.—During the past two or three years, with greater requirements for the use of the optical pyrometer we are getting many thousands of readings during the year. In the pouring temperatures, we have considerable use for the optical pyrometers but in their more extended use we have taken away from the pourer an idea as to the true temperature of that metal. That is, he becomes so dependent on the optical pyrometer that when the pyrometer goes bad—and they all do with the best of checking and with the best of care—you are frequently "up against it" for the pourer has become so dependent on it that he mispours on a series of castings. The optical pyrometer has a definite place and it is used in our plant for the purpose of controlling the melting temperature. We are operating on pulverized coal and, learning the first tap as taken by the optical pyrometer, we can cut back our furnace very definitely and in this way the operation becomes more mechanical; but we have realized that the pourer really needs a practical knowledge of the pouring temperatures.

George A. Orrok.—When you have an instrument, even when it is not a very good instrument, you can control your temperature much closer than is possible by eye; that is true in any process where combustion is taking place.

A. L. Feild.—I do not believe that practical steelmakers will agree to the statement that melting temperatures cannot be estimated within 150° by ordinary visual observation. It is more probable that an experienced melter can control the average temperature of the steel bath within close limits, say, 10° or 15° C. It should be remembered that an optical pyrometer measures the temperature of a very small area within the furnace. The average furnace temperature can be obtained only from a large number of readings and this average temperature does not correspond to the average temperature of the metal bath beneath the slag.

L. F. Reinartz,† Middletown, Ohio.—In answer to the statement that all ingots should be solid and have no blowholes, I wish to say that

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† Assistant General Superintendent, American Rolling Mill Co.

it depends entirely on the use that is to be made of the steel. Steelmakers for many years have known that, for certain purposes, effervescing steel is preferable to an absolutely killed steel; provided that such steel is properly finished in the furnace. As to whether high manganese in low-carbon steel has some deleterious effect on the steel I do not know; but I do know that when we are normally operating on a 0.35 to 0.45 per cent. manganese and 0.120 per cent. carbon steel, and we get a 0.50 per cent. manganese we are very apt to have a rising steel, provided the same amount of deoxidizer has been used in both heats.

Henri Le Chatelier, Paris, France (written discussion*).—It is always useful to apply exact figures to industrial operations, even when they can be conveniently carried on by a simple routine. In fact, the writer believes that measuring temperatures in open-hearth furnaces may be very useful in the operation of making steel. The disappearing-filament pyrometer is a simple enough method to be put into the hands of any shop foreman, or even of the ordinary workman.

It is true that some furnacemen have an extraordinary facility for knowing exactly the right moment for casting the steel. By watching the solidification in the test mold, the rate of melting of the stirring rod, the fracture of the skull, they deduce the state of the steel bath. But this empirical faculty cannot be taught; some have it and some do not. On the other hand, measurements of temperature can be made by any one.

Exact determination of the pouring temperature of the steel as it comes from the furnace is difficult, if not impossible, because the temperature is not uniform throughout the furnace. The surface layers are hotter than those deeper in the bath; the temperature of the pouring stream generally rises during tapping (the variation may be 50°) it is not possible to have all the tapping done at the highest temperature. But the mixing of the metal as it mingles in the ladle remedies that difficulty. The only important thing, in fact, is the temperature in the ladle.

The size and shape of the crystallites that develop during the solidification of the steel certainly have a great influence on the properties of the metal; these depend on many factors, of which the temperature is among the most important, and this effect of temperature is not easy to explain. The longer the metal has been melted at a high temperature, the larger and more regular will be these crystallites. The effect of temperature is particularly marked in the solidification of bronze containing 10 per cent. of tin. A variation of 100° in the melting temperature causes such great differences in the texture of the alloy that the results appear to be two different substances.

Agitation has an equally great effect. It brings about a mixed crystallization that generally is advantageous. The fall of the metal into

* Translated from the French.

the mold produces a puddling that disappears little by little. The hotter the metal, the longer is the time that elapses before the beginning of solidification, which gives the interior movements a longer time in which to stop. Hence it is difficult to separate the influence of temperature from that of agitation. They are, nevertheless, two distinct and important elementary factors in the crystallization of ingots.

WILLIAM J. PRIESTLEY,* Pittsburgh, Pa. (written discussion).—The temperature figures apply only to ingots; steel temperatures for castings would be higher. The effect of temperature in casting is very evident as steel of exactly the same chemical analysis, made in the same manner, and cast in the same size molds will behave well in one instance and badly in another. The only apparent difference is the temperature at which it is cast in the mold. We have all seen this occur in both deoxidized and effervescing steel. A fourth factor in determining what a batch of steel will be after casting that might have been mentioned is the rate of cooling the steel in the mold.

I was particularly interested in this subject on account of the work we are doing with ferroalloys; the behavior of the various elements with one another is governed in a large degree by the temperatures at which they are brought together. The reactions in many instances are more truly physical than chemical.

I have searched my files for actual data on casting temperatures to compare with the "assumed finishing temperatures" given in this paper; as far as I know, the steel represented by these actual figures made good ingots. In most cases, the temperatures are lower than those in the paper but they are close enough to show the practical value of the author's systematic gradations of temperatures, for varying carbon contents. Also, as he suggests, modifications may have to be made for varying conditions of composition, teeming and mold sizes. The actual temperatures were as follows; the differences from the author's figures are shown in parentheses:

Kind	Per Cent. Carbon	Tapping Temperature, Entering Ladle, Degrees C.	Teeming Temperatures		Average Variation from Author's Figures, Degrees C.
			Beginning, Degrees C.	End, Degrees C.	
Effervescing	0.15	1575(−35)	1525(−50)	1500(−45)	−43
Effervescing	0.15	1605(−5)	1550(−25)	1535(−10)	−13
Deoxidized	0.22	1575(−18)	1525(−33)	1500(−38)	−29
Deoxidized	0.25	1565(−35)	1525(−40)	1510(−25)	−33
Deoxidized	0.38	1565(−22)	1525(−27)	1505(−17)	−22
Deoxidized	0.87	1550(+12)	1490(−13)	1475(+2)	−0

* Metallurgical Engineer, Electromet. Sales Corpn.

As an instance of how these theoretical temperatures may have to be raised or lowered, depending on the nature of the work, I submit for comparison some actual temperatures obtained from pouring acid open-hearth steel into a particular kind of casting.

	Per Cent. Carbon	Tapping Temperatures Entering Ladle, Degrees C.	Teeming Temperature Beginning, Degrees C.	Teeming Temperature End, Degrees C.
Actual	0.30	1630	1490	1500
Theoretical	0.30	1595	1560	1530

The extreme drop from tapping to beginning of pouring is probably due to the length of time the steel was held in the ladle, the metal near the bottom being chilled and that at the top of the ladle under the slag being hotter.

There are conditions under which an excessively hot steel, even in the furnace, may be detrimental; the steel should be no hotter than required to flux out readily the products of oxidation, in the form of non-metallic inclusions. When selecting deoxidizers, or scavengers, suitable combinations should be chosen so as to form complex slags of the lowest melting points that will rise most effectively out of the molten bath of steel. Many excellent deoxidizers do not have slag-forming properties, and unless they are combined with other agents, will remain in the steel regardless of temperature. As extremely hot steel has a greater solvent power for gases than steel at a lower temperature, the reason is obvious why a temperature higher than that required to clean the steel from non-metallic inclusions is unnecessary and even harmful in instances where residual silicon and manganese are high.

The author attributes the failure of the low-carbon steels to effervesce when excessively hot to the manganese in low-carbon effervescing steel where silicon is not present. The same thing would occur, perhaps to a more pronounced degree, if residual silicon were present and a growing ingot would be the result. Foundrymen will also observe some difficulties in trying to kill an excessively hot steel that contains high residual silicon.

H. W. Gillett,* Washington, D. C. (written discussion).—It is to be hoped that the object of this paper—to bring to light quantitative data on finishing temperatures—will be attained in the discussion. Such data exist and should make it unnecessary to go back to 1882. At the Charleston Naval Ordnance plant, temperatures of the tap and of the ladle stream were taken steadily for four years and were considered indispensable. One modern alloy-steel plant has an optical pyrometer in this service 24 hr. a day. This plant, and others, are actively looking for a means for measuring the temperature of the steel in the furnace below the

* Chief, Div. of Metallurgy, Bureau of Standards.

slag. They realize that for actual furnace control the "ample experience" and "good judgment" mentioned must still be called upon, but find it an advantage to check the melter's judgment by determining tapping temperatures. They look forward to the time when they can shorten the period of training a new melter by teaching him in a day or a week to handle a pyrometer and turn out heats at a predetermined temperature, instead of waiting ten years for his experience and judgment to mature.

Modern makers of quality steel are not so pessimistic about actual temperature measurements as is the author. Competent American steelmakers question the allegation that foreign practice or gun steel involves "excessively" high temperatures; until both foreign and American practice can be reported in degrees, instead of "assumed" degrees, or by adjectives, the question will remain open.

Many minor statements are open to question or to qualification. Are iron sulfide and ferrous oxide soluble in iron? Are manganese sulfide and manganese oxide insoluble? Is carbon "undoubtedly in combination" in molten steel? Does metal have a greater solvent power for gases the higher the temperature? Is the gas in the skin holes hydrogen? Lowering of the melting point will rarely be directly proportional to alloy content. Rumelin and Nick[2] find the lowering due to manganese double that stated by the author, though the difference is negligible.

Popp[3] has given data on about 100 heats from 40-ton furnaces at the August-Thyssen-Hütte. He used an optical pyrometer, his corrections for deviation from black body conditions are within 2° C. of those given by Burgess.[4] The average temperatures measured by Popp differ considerably from those assumed by Hibbard. Instead of a 50° difference between tapping and mean teeming temperatures, Popp finds an average of 35°. For 0.10 per cent. carbon steel, Hibbard's mean teeming temperature is 1565°; Popp's 1645°, a difference of 80°. For 0.20 per cent. carbon, Hibbard's temperature is 1555°, Popp's, 1620°, a difference of 70°. For 0.30 per cent. carbon, Hibbard's temperature is 1545°; Popp's, 1590°, a difference of 45°. The time from tapping to teeming ran from 6 to 8 min., *i. e.*, closely the same as that assumed by Hibbard for Table 1. Teeming took 15 to 20 min. from the 40-ton furnaces against Hibbard's assumption of 30 min. for a 50-ton furnace. Popp finds that with a suitable slag layer on the ladle, the teeming temperatures actually rise, at least up to a period of around 20 min. instead of falling; his explanation

[2] *Ferrum* (1915) **12**, 41.

[3] C. Popp: Abstich—und Vergiesstemperaturen von Martinstahlschmelzungen. *Ber. der Fachausschüsse des Vereins deutscher Eisenhüttenleute* (July 17, 1924), Bericht Nr. 46.

[4] G. K. Burgess: Temperature Measurements in Bessemer and Open-hearth Practice. Bur. of Stand. *Tech. Paper* 91.

agrees with that put forth by Hibbard to explain his small assumed temperature drop in the ladle.

The differences between the Popp and the Hibbard temperatures for the stream entering the ladle on tapping, for 0.10, 0.20, and 0.30 per cent. carbon, 65°, 50°, and 30° C. Hibbard's temperatures, plotted against carbon content, give over this range a line parallel to the melting point curve, while Popp's show a greater temperature interval, the lower the carbon. Conversely, at higher carbon content, extrapolation of Popp's data would indicate a better agreement with Hibbard's assumptions than at the low carbon. It is reasonable to suppose that there is not really 50° to 70° C. difference between the average finishing temperature of a 0.20 per cent. carbon steel in Germany and in the United States.

I. A. Billiar, Burnham, Pa. (written discussion).—While I agree that tapping and teeming temperatures are important, I do not believe that a variation of 20° F. can be shown to make steel "off" in quality. The manufacture of steel is not such an exact science that such small variations in temperatures have any influence on the quality of the final product.

More killed steel is injured by improper manipulation of the bath than by small variations in casting temperatures. Practices, such as melting heats too low in carbon to have ample time for refining, in order to cut down the time per heat, oreing a heat almost to tapping time, using coal or coke in the ladle and using large quantities (100 lb. to a 60-ton heat) of aluminum in the ladle are more likely to result in lower quality products than a reasonable variation in casting temperatures—say 50° F. plus or minus from the ideal established in each plant.

In Tables 2 and 3 are shown data on twenty acid heats taken at random from our files. The charges are 130,000 lb. in 55-ton furnaces, tapped into cold ladles and held 10 to 30 min., depending on tapping temperatures. This interval is taken from the time the slag starts to run over the lip of the ladle. The 55-ton ladles have a lining varying from 7 in. thick at the top to 11 in. thick at the bottom and 9 in. of brick over the bottom; 2-in. nozzles are used and all steels are top poured. About 1000 to 2000 lb. of skull remains in the ladle after teeming, which takes 35 to 75 min. depending on the number of ingots. Fifty per cent. ferrosilicon and 80 per cent. ferromanganese are added in the furnace and fuel and air are shut off about 20 to 25 min. before tapping. Slag temperatures are taken immediately after shutting off the fuel and before additions are made.

The large drop from tapping temperature to teeming temperature is due to tapping into a cold ladle with a heavy lining and also to the length of time the heat is held in the ladle. After the heavy lining is thoroughly heated by the steel the drop in temperature is slow, averaging 65° F.

during teeming, which is not far from the author's allowable drop, although he assumes, in Table 1, that teeming takes 30 min., while our time will average 50 min. Our average tapping temperatures for 0.70 and 0.48 per cent. carbon steel agree almost exactly with those shown in Table 1, but our teeming temperatures are considerably lower.

The author recommends that the tapping temperatures should vary to compensate for a large or small charge. This has not been our experience. We tap 90-ton heats at the same temperature as the 55-ton heats, and find temperatures during teeming to be about the same as on the smaller heats.

I have never been able to detect any variation in the behavior of the ingots in the press or rolls that might be traced to a difference in casting temperature of 50° F. from our average. In other words, an 8200-lb. ingot teemed in 2½ min. at our average temperature of 2675° F. and a similar ingot teemed in the same time at 2625° F. will not show any difference in skin defects. If the heat has been properly made neither should show any defects when rolled or pressed. Teeming speed is of more importance in the elimination of skin defects. We have repeatedly teemed alternative ingots from the same heat at high and low rates of speed and carefully compared results after blooming; the faster poured ingots always showed more skin defects.

I have never been able to notice any difference in physical properties due to 50° F. difference in casting temperatures. Physical tests from

TABLE 2

Furnace charge 130,000-lb. acid steel, top poured through two 2-in. nozzles; average final analysis, carbon 0.70 per cent., silicon 0.22 per cent., manganese 0.66 per cent.

	Temperature, Degrees F.					Teeming Time, Min.	Number of Ingots Poured	Per Cent. Carbon
	Slag in Furnace 25 Min. Before Tapping	Tapping, Entering Ladle	Teeming, Beginning	Teeming, End	Minutes Held in Ladle			
1	3035	2880	2720	2610	15	64	145	0.69
2	3105	2880	2690	2625	15	38	111	0.73
3	3025	2850	2670	2600	15	48	154	0.72
4	3025	2860	2690	2600	15	44	115	0.66
5	3060	2865	2650	2580	14	52	122	0.72
6	3020	2860	2670	2625	18	53	125	0.70
7	2980	2790	2650	2600	10	49	113	0.75
8	3045	2850	2690	2610	15	45	122	0.67
9	3025	2840	2690	2625	11	43	129	0.75
10	3025	2810	2650	2600	15	47	79	0.67
Ave......	3035	2849	2677	2608	14	48	121	0.70

final heat-treated products or from specially made test ingots do not show variations that can be traced to variations in casting temperatures.

I agree that the use of a pyrometer to tell the temperature of the open-hearth bath metal is of doubtful value.

TABLE 3

Furnace charge 130,000 lb. acid steel, top poured through one 2-in. nozzle; average final analysis, carbon 0.477 per cent., silicon 0.20 per cent., manganese 0.60 per cent.

	Temperature, Degrees F.					Teeming Time, Min.	Number of Ingots Poured	Per Cent. Carbon
	Slag in Furnace 25 Min. Before Tapping	Tapping, Entering Ladle	Teeming, Beginning	Teeming, End	Minutes Held in Ladle			
1	3080	2880	2690	2615	15	58	18	0.48
2	3075	2880	2650	2600	20	61	15	0.45
3	3060	2880	2710	2610	20	71	15	0.46
4	3130	2880	2670	2600	20	63	15	0.48
5	3045	2810	2650	2610	15	53	15	0.45
6	3045	2830	2650	2580	15	62	15	0.48
7	3075	2890	2690	2625	18	41	15	0.46
8	3025	2850	2690	2580	14	45	15	0.55
9	3090	2930	2680	2610	30	55	15	0.48
10	3030	2880	2680	2610	15	50	15	0.48
Ave......	3065	2871	2676	2604	18	56	15	0.477

All except No. 1 poured into 23-in. round molds with round corrugations; weight of mold 15,000 lb. Weight of ingot 8,200 lb.

W. P. BARBA, Philadelphia, Pa. (written discussion).—The author says: "Three things largely determine what a batch of steel really will be; viz., composition, casting temperature, and rate of teeming." Composition should include the degree of refinement, all of which was fully discussed by Doctor Howe and the writer in a paper[5] read in 1922. Casting temperature, joined with rate of teeming, is a very mixed problem, involving elements of composition, refinement, size of ingot mold, shape and character of ingot mold, method of pouring (that is, top or bottom), and the casting temperature chosen out of these varying elements cannot be stated in terms of degrees of temperature for anything except one particular set of these conditions. Rate of teeming, and consequent casting temperature within the ingot, which alone is important, should be regulated by the judgment of the man in charge of pouring, carefully

[5] Acid Open-hearth Process for Manufacture of Gun Steels and Fine Steels. *Trans.* (1922) 67, 172.

observing and judging all these conditions from the appearance of the metal as it rises in the mold. Therefore, within the problem of making a good ingot, casting temperature is perhaps one of the widest permissible variables and should not be sought to be governed by a fixed pyrometric measurement of temperature.

It is true, as mentioned in the third paragraph, that most results hitherto reported "demonstrate the efficiency of pyrometers used rather than aid the steelmaker." In this connection, one is reminded of the early days of pyrometers used for measuring temperatures of steel in heating furnaces, when the revered William Metcalf, much doubting the then efficiency of any pyrometer offered, ventured the statement that "the God-given pyrometer, the eye, was much the most sensitive and dependable when properly educated." This is supported by parallel work when the microscope entered the field of iron and steel metallography, because those of us who were interested in the pioneer stages of the application of the microscope found that it was necessary to make many, many thousands of observations before lines of incidence could be observed and deductions drawn. Much the same situation presents itself on pyrometric observations of pouring temperatures of steel, and the contributing and collateral data are even more important for close observations and recording in a well worked out daily log of each heat and operation than is the mere recording of an observed pyrometric temperature.

Under the caption Pouring Temperatures, the paragraph beginning "The effect of temperature on crystallization," the author has well stated truths, whose elements have been carefully worked out. But, in the first paragraph on page 478, the author's claim that "there is little if any segregation" should not be taken as dogmatic, because the size of the ingot, the chemistry of the steel as concerns much or little mass of segregating elements, and the degree of control of pouring, as many times described, will greatly affect the truth of such a statement concerning segregation. One might call attention to an oft-stated ideal condition of pouring by repeating: "The ideal temperature for casting a good ingot is to have matters so arranged that the ingot is filled with fluid metal during one second of time, and completely solidified, though not chilled, during the next succeeding second of time, and that any departure from this ideal, impossible result, is a modification of the ideal."

To sum up, careful recording of vital elements in each heat of steel, checking these through the further manufacture to the point of ultimate use, governed by the exercise of good judgment based on wide experience and many recorded and investigated observations are essential, whether assisted by a pyrometer or heat observation, or not. To this, it is proper to add that, like the microscope, the pyrometer is coming more and more to supplement and supplant judgment by scientific records.

Perhaps it is appropriate to state that on pages 481, 482, and 483, the use of history from a bibliography not too fresh is given greater authority than today it might be thought to deserve.

JEROME STRAUSS,* Washington, D. C. (written discussion).—Discussion of actual melting and pouring temperatures, in the hope that through it means will be found for the transfer of an ideal practice for a given material from one manufacturing plant to another, seems to strike far from the mark when, in shop practice, there is no means for readily measuring those temperatures with the degree of precision required. The author speaks of ideal temperatures and then lays great stress on the value of qualitative tests that serve as indices of temperature but are not capable of translation into actual temperature values. If a temperature difference of 10° is sufficient to differentiate between normal and off quality metal, devices of so much greater sensitivity (to say nothing of accuracy) than we possess must be developed, that the general application of such measurements in steelmaking lies far in the future. Because of the 30° temperature fall between the first and last ingot of the author's average heat, two-thirds of each melt must be of off quality. By the same token, the top and bottom of a large ingot, such as an armor-plate ingot, must be of vastly different character as a result of temperature effects alone. Much proof must be forthcoming before such statements can be generally accepted.

The important factor, from the viewpoint of the steelmaker, in so far as pouring and teeming practices are concerned, is not the actual temperature of the bath or the stream of molten metal but rather the difference between those temperatures and the solidification range of the metal. These differences are measurable with a precision satisfactory for the purpose by means of the spoon test (setting time). This test is considered to be of more value than any of the other tests mentioned or with which the writer is acquainted, being affected only by the temperature of the spoon, the thickness of the film of slag obtained on the spoon before sampling, and the temperature of the atmosphere in the vicinity of the furnace. When practice in any one shop has been standardized, the effect of these variables, as judged by the character of the cast metal, is so small as to be unobservable.

The author has used the word "quality" rather recklessly and with presumably different meanings. Quality as determined by the absence of surface defects and pipe in the rolled product or quality as measured by ability to obtain, either normalized or after heat treatment, longitudinal tensile and impact results of a predetermined magnitude, is far different from quality as required in the form of uniform strength and ductility in all directions such as in structures subjected to high transverse stresses, both static and dynamic. The use of this term indiscriminately without

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qualification, in reference to such widely different material as plate steels, automotive steels, and steels for ordnance construction is indeed to be discouraged.

From the standpoint of the extremely high requirements demanded, material for ordnance construction forms a class in which the temperature of the metal entering the mold is a vital factor. Many other variables of the steel-making process may be slighted to an appreciable degree and yet yield a product closely approaching the best, if the teeming temperature is low and solidification rapid. Even with steels of about 0.5 per cent. carbon, which are frequently used for these purposes, it is difficult to see how a high pouring temperature (quoted by the author from Caspersson's work) would produce "quality" metal. Perhaps crucible steel of good grade can be obtained from molten metal that is excessively hot but the ingots are unusually small and solidification most rapid; nevertheless, it must be proved that such metal is not poorer than that poured at a lower temperature but produced under otherwise like conditions. True enough, a long time in the mold in the molten state will permit the steel to disgorge non-metallic particles formed while cooling and those mechanically dragged into the mold with the metal and also permit the formation of an extensive pipe, even in big-end up, hot-topped ingots. But are these effects alone, indications of high quality? Is it not better to permit mechanically entrapped non-metallic masses and those formed during a large portion of the cooling in the molten state to separate in the ladle? Great objections have been made by many whose operations are on other than a tonnage basis alone to the practice "making steel in the ladle;" it would seem to be going from bad to worse to have avoidable steel-making reactions taking place in the mold. It has frequently been demonstrated, in the writer's work, that serious troubles arise from those non-metallic particles that separate from the liquid metal, and to some extent combine with one another, during passage of the metal through the solidification range. Undoubtedly great changes of solubility occur during this period (probably more than in an equivalent temperature drop above the liquidus) and the particles so separated have little time to escape from between growing crystalline masses, through a very viscous liquid. The use of a high pouring temperature will lengthen the time taken by the molten mass in cooling from the liquidus to the solidus, thereby permitting these precipitated materials to separate more completely from the solvent and to accumulate into massive continuous films. Rapid cooling by pouring from a relatively low temperature into a mold at ordinary temperature largely prevents their separation and agglomeration in a degree varying with the size of the ingot and with the mold design. It would seem desirable, therefore, and this practice has proved eminently satisfactory, to tap steel from the furnace into the ladle at a temperature sufficient to permit holding in

the ladle as long as possible, without formation of a skull so thick as to make pouring difficult, and still leave the metal at such temperature that it may be tapped into the mold at the desired rate and provide just a slight margin of safety between the temperature of the metal stream at the end of pouring and the temperature of initial solidification.

It is desirable, from a quality standpoint, to permit cooling to occur in the ladle rather than in the furnace. Although the slag condition in the furnace may be such as to help free the metal from objectionable impurities, other impurities are constantly being transferred to the bath by reaction with the hot furnace hearth; even in a highly heated ladle, a thin film of solid steel first forms, protecting the metal from reaction with the lining and, in contact where obtained, the much lower temperature of the ladle lining as compared with the furnace hearth makes appreciable reaction with the metal far less likely.

In brief, there are many factors influencing the physical characteristics of a steel ingot. For the very highest performance of the product, all of these influences must be subjected to the most careful control that available knowledge and appliances will permit. However, small variations of pouring temperature seem to exert a greater effect than changes of a relatively similar magnitude in the other factors. While it is desirable to cause the separation of those gases, oxides, sulfides, etc. and their reaction products, that are generally considered to be detrimental to steel, such amounts as tend to separate in the solidification range are most probably less harmful when retained in solution than when in the form of intergranular particles and films. Practices that tend toward this end, through the use of low pouring temperatures and high solidification rates, are productive of true quality.

HARRY H. SMITH,* New York, N. Y. (written discussion).—It is indeed difficult to determine, with any degree of accuracy, the temperatures of open-hearth steel while in the furnace, being tapped into ladle, or teemed into molds. The slag in the furnace and the burning gases, while the steel is being tapped or teemed, offer serious obstacles to the determination of accurate temperatures by means of the optical pyrometer. Difficulty of installation has kept other forms of pyrometers from being used to any extent.

The accurate temperature of the steel, fortunately, is not necessary to produce first-class steel, as each heat is tested by means of "fracture" and "spoon tests" for approximate carbon analysis and fluidity of the metal respectively. Inasmuch as most heats vary in some detail in chemical analysis, the best temperature for tapping each heat also varies. Accordingly the determination of the fluidity of the metal by the spoon test, that is, the way it clears the spoon, seems to be the best practical method of determining whether the heat will teem satisfactorily.

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Whether or not the steel has been made satisfactorily can best be determined after the steel has been semi-finished; that is, in the form of billets or bars. The problem then is to determine, in the case of a bad heat, just what operation has been responsible for the failure of the steel to pass the necessary tests.

Beside the furnace and teeming operations, it is necessary to use proper kind of ingot molds and to have proper soaking-pit conditions. Ingot molds of various types have been known to yield different quality of steel billets or bars from the same heat. At one plant, better steel has been produced by using a fluted mold instead of the usual tapered rectangular or square mold; while by using similar molds at another plant the opposite results were obtained. The type of mold also controls, to a large extent, the rate of cooling of the steel.

The overheating or burning of the ingots while in the soaking pits and the rolling of ingots at too low a temperature have caused many heats that had been properly made and teemed to be condemned. A certain definite type of equipment and plan of procedure must be determined for each operation in each plant in order to secure best results.

Henry D. Hibbard (author's reply to discussion).—The paper is not a discussion of processes but deals with the finishing temperatures of steels as they are actually made, whether properly or not. The author agrees that ofttimes steel should be made better than it is.

As for training the eye to the work, it may be said that no steel melter depends on his eye alone for governing temperature; other things, mentioned in the paper, help him.

Table 1 is, in aim, ideal. Wider variations in temperature may admittedly be allowed in ordinary practice without disaster. By the term "off," the author does not mean that the steel is ruined but only that its mechanical properties are inferior to what they would be were the finishing temperatures within the ideal limits. Particularly, it would have less ductility and lower rating in the impact test.

When compiling the table, the author did not have the fusion temperatures of iron containing silicon or manganese, separately or together. He only aimed to get within 10° C.; the assumptions as to the effects of those elements would probably not introduce an error greater than that. If, however, Messrs. Zimermann and Feild think the qualified assumptions in this connection to be unwarranted, let them tell what the effects are of 0.2 per cent. of silicon and 0.6 per cent. of manganese on the fusion point of simple steel. The fusion points of the iron-manganese system, now being determined by the Bureau of Standards, will indeed be welcome.

Since the table was made the author has compared it with operating temperatures in steelworks; there were discrepancies but the average results agreed fairly well with the table. Other tables may be made up

and used by any one, for steel castings, large ingots, or alloy steels, but if we can agree on one for the steels and conditions considered in the paper, we will have a good starting point for the others.

What Messrs. Barba and Styri define as refining, the author would consider as comprehended by what he termed composition: not, indeed, in the usual ultimate analysis but using the term to take in every ingredient in the metal without exception and whether determined or not. Mr. Styri has criticized the steel-making processes alluded to and, though not germane to the subject, it may be worth while to consider the criticisms briefly. He calls killed steels well made and then says that they are not all good. In fact, the worst steel the author ever saw was killed. It is easy to kill steel, but that alone gives it no claim to quality. The claim that partly killed steels are poorly made, though usually true, cannot be universally accepted as some serve their purpose as well if not better than if they were completely killed. Then he calls effervescing steels rotten. The author asks how else he would make steel for boiler plate, which, rolled direct, would stretch from 30 to 35 per cent. in 8 in. in the tensile test; and how else steel to make sheets with clean, smooth good-looking surfaces; and how else steel for welded pipes? Millions of tons per year of effervescing steel are made for each of these purposes. Effervescing steels were, indeed, made 40 years ago and, in the author's opinion, will be for 40 years to come, because when properly made, they are best for certain purposes. He will go so far as to admit and insist that no steel whatever should rise in the mold after teeming; when it does it is always inferior. The all-around steelmaker must be able to make the kind of steel wanted, which is determined by many conditions, and not by the single one of prevention of gasholes.

Mr. Styri's speculations as to insufficient degree of heat in the past have no foundation. Forty years ago, it was as easy to attain in a steel furnace the highest temperature the silica brick would stand as it is now.

In the absence of analyses of the gases in the different kinds of gasholes in steel, which are sorely needed, the author has always been careful to state only the probability that hydrogen is the chief ingredient of skin-hole gas.

Balancing all the remarks and criticisms contributed, the author sees no reason for modifying Table 1 at present, but the field is open for any one to offer one more nearly correct. If data therefor exist, this surely ought to be done.

Manufacture of Ferrophosphorus at Rockdale, Tenn.

By James A. Barr,* Mt. Pleasant, Tenn.

(Birmingham Meeting, October, 1924)

Ferrophosphorus, an alloy of phosphorus and iron or perhaps a physical mixture of definite compounds of iron and phosphorus, has become of increasing importance as the use of the basic open hearth has extended. Commercial ferrophosphorus is a porous, brittle metal of crystalline structure and often with a bluish metallic luster. A typical analysis is as follows:

	Per Cent.	
Phosphorus	18.0 to	22.0
Iron	80.0	76.0
Oxygen	0.2	
Sulfur	0.3	
Silicon	0.1	
Carbon	0.1	
Manganese	0.2	

This alloy was first made in an electric furnace, as it was thought that the high heat of the electric arc together with the reductive effect of carbon was necessary.

About 1898, J. J. Gray, Jr., was producing a high-phosphorus pig iron in his furnace at Rockdale, Tenn., by using high-phosphorus, local iron ores. As these high-phosphorus ores were difficult to obtain, he conceived the idea of increasing the phosphorus content of the pig iron by the addition of phosphate rock to the furnace burden. When the phosphorus content of the pig was kept low and only small amounts of phosphate rock were added to the burden, no particular troubles were encountered, but when he increased the amount of phosphate rock to produce an 18 per cent. alloy, his furnace troubles rapidly multiplied. After many failures and freeze-ups, he was partly successful in making short campaigns on 18 to 20 per cent. "ferro."

At first, when the furnace got in bad shape on ferro, he would switch to a regular pig-iron burden until the furnace was brought around sufficiently to start on ferro again. About this time, Mr. Gray applied for and obtained his first patent.

As he grew more skilled in the furnace operations, he was enabled to extend the furnace campaigns and produce ferrophosphorus continuously for the life of the furnace lining. These improvements were made the subject of another patent issued in 1916.

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Essentially, ferrophosphorus is the result of smelting a mixture of iron ore, phosphatic rock, siliceous flux and coke, under intensely reducing furnace conditions, with heated blast, above a bath of molten slag and ferrophosphorus.

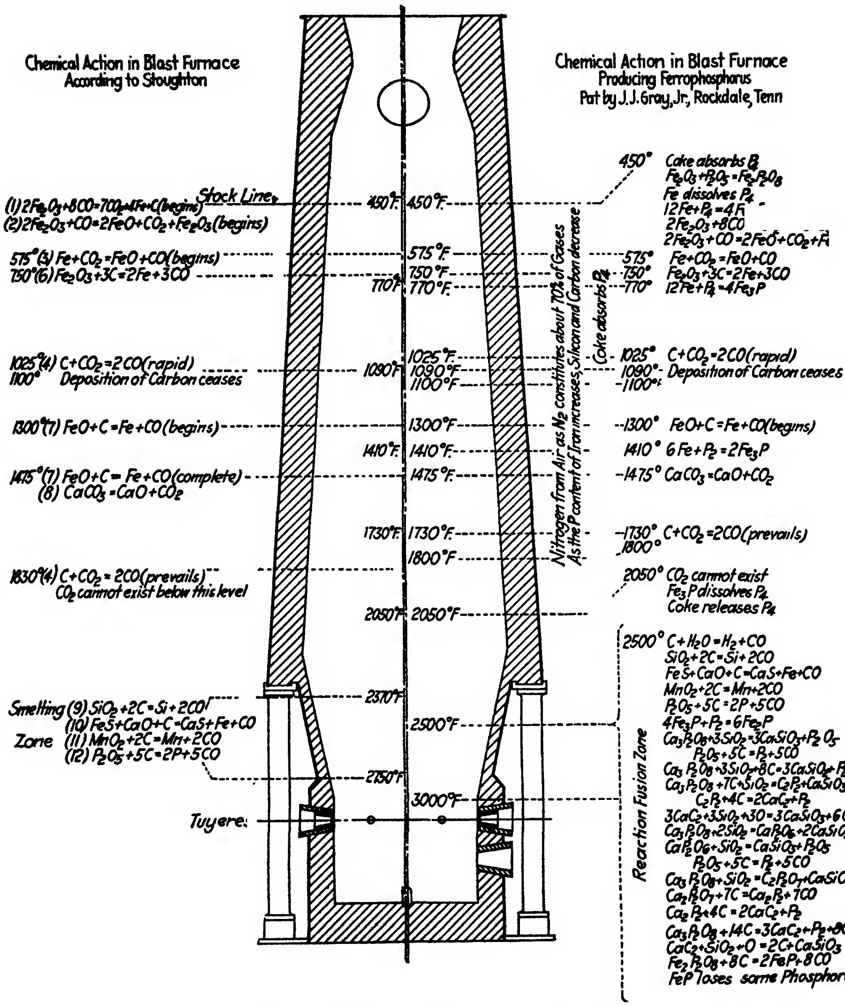

FIG. 1.—BLAST FURNACE REACTIONS.

The iron ore, a limonite, is obtained from Mr. Gray's mine, 50 miles south on the Louisville & Nashville Railroad, at Iron City. The ore is a nodular variety occurring in a clay matrix. The beds are stripped and mined by steam shovels, hauled by side-dump cars and locomotives to washers, where the clay is washed out in log washers and trommels, followed by McClanahan-Stone jigs for the separation of flint. The

concentrated ore runs about as follows: Iron 45 per cent., silica 10 per cent., phosphorus 2 per cent. Silica flux is obtained from jig tailings, which run quite high in iron as well as silica. Sometimes small amounts of washed sand and gravel, from Spruce Pine, Ala., are used.

Phosphate rock, in the lump form, is obtained from the Mt. Pleasant field about 6 miles to the north; a large firm lump being preferred, running high in BPL ($Ca_3P_2O_8$) and low in free lime. A typical analysis is:

	Per Cent.
$Ca_3P_2O_8$	76.0 to 78.0
Equivalent to P	15.2 to 15.6
SiO_2	4.5
Free lime, $CaCO_3$	5.0

Other materials may be used in the furnace burden, such as mill cinder, running high in iron and silica, iron turnings, scrap pig, and shot ferrophosphorus from the magnetic separating plant.

A good firm grade of coke is used and the braize is screened out in the usual manner. The presence of too much fines in the burden tends to form scaffolds and make the furnace slip.

All the incoming materials are brought in on a high line from L. & N. connections and dumped from a trestle into a concrete tunnel, in which a charge car, with a multiple-scale beam, operates to collect the furnace charge. The charges are dumped into a skip, hoisted on an incline track, and end-dumped through a single-bell top into the furnace. The furnace has the following dimensions: Height 40 ft., inside hearth diameter 8 ft., bosh diameter 12 ft., bosh angle 80°.

The hearth and bosh are water-cooled, as the molten charge is very corrosive and would soon cut its way through an uncooled jacket and lining. Six water-cooled bronze tuyeres are connected through the usual penstocks and nozzles to a brick-lined bustle pipe, which distributes the blast.

The furnace gases are handled at about 450° to 500° in a brick-lined downcomer through two dust catchers into a cast-iron balloon gas washer; the flue dust is wasted.

A battery of four checker-filled single-pass stoves use part of the furnace gas to heat the blast to around 1000° F.

The remainder of the gas, and there is a large excess over the usual iron blast furnace quantities, is burned under a battery of Rust water-tube boilers, which supply steam for blowing engines, pumps, and general purposes.

Blast is furnished by a McClanahan-Stone, horizontal, poppet-valve engine of very early manufacture, but still giving excellent service. It is equipped with leather flap valves, a forerunner of the modern plate valve; the cylinder is 6 by 6 ft. and when run at the usual 24 r.p.m. furnishes 7200 cu. ft. free air per minute at 12 to 15 lb. pressure. A smaller vertical

Weimer blowing engine is kept in reserve. The proper manipulation of blast volume is very important. Too much air causes the melting line to rise, tends to form scaffolds, and burns coke needed for the reduction of phosphorus.

The usual operating procedure is to add five regular charges consisting of: Phosphate rock, iron ore or mill cinder, high-silica tailing, shot ferrophosphorus, coke—about twice amount used in pig-iron practice.

Every fifth time, a regular pig-iron charge is added to help keep the furnace working freely and consists of iron ore, limestone and coke. Sometimes a blank coke charge is added in addition to the above, according to the needs of the furnace.

Slag is tapped every 3 hr., into a water-filled granulating pit. The following analysis is typical:

	Per Cent.		Per Cent.
Al_2O_3	5.18	P_2O_5	7.33
SiO_2	43.59	S	1.07
CaO	35.18	MnO	0.54
FeO	4.96		

The ferrophosphorus is tapped every 6 hr. and run on to a floor paved with cast-iron bricks, where it cools in thin slabs and can be easily broken and handled. At the end of the cast, when the iron notch is blown free of slag by blast pressure, the presence of lumps of incandescent coke is very noticeable and shows that it is present in the tuyere zone to effect the reduction of the phosphorus.

The capacity of the furnace is 35 tons of ferro per 24 hr. or about half that of usual pig-iron production.

Some phosphorus oozes out of the cracks in the jacket and collects under water. During the war, this was scraped up and sold. Occasionally white fumes of phosphorus burning to P_2O_5 can be seen. Some of the phosphorus is lost in the stack gases and the remainder in the slag. The problem of saving P_2O_5 from blast-furnace gases is complicated by the large volume, *i. e.*, about five times that from an electric furnace.

As the slag contains considerable shot ferrophosphorus, provisions are made for its recovery. The slag is dipped from the granulating pit by a bucket-operating locomotive crane and dumped on to a drainage pile and finally fed by the same crane into a hopper located over the feed of a 5 by 40-ft. direct-heat, countercurrent, rotary dryer. The dried slag is elevated and discharged on to a Dings belt-type magnetic separator. The reclaimed slag is fed back with the furnace burden as previously described. The rejected slag is chuted directly into railroad cars for use as ballast.

Ferrophosphorus is mainly used for increasing the phosphorus content of steel and is added directly to the ladle The writer observed one

steel company adding 650 lb. to the 100-ton ladle. As is well known, the basic open hearth removes practically all of the phosphorus from the steel. When rolling thin sheets it has been found that a small percentage of phosphorus is necessary in the steel to make the sheets strip readily. Certain other classes of steel also require small amounts of phosphorus in exact quantities. Ferrophosphorus may also be added to a cupola charge where the pig is too low in phosphorus for the casting requirements.

Some Factors Affecting the Elimination of Sulfur in the Basic Open-hearth Process

By C. H. Herty,* Jr., A. R. Belyea, E. H. Burkart, and C. C. Miller,† Lackawanna, N. Y.

(New York Meeting, February, 1925)

The removal of sulfur from steel has been studied by many investigators, but the quantitative relationships between the factors involved have not been determined. This is undoubtedly due to the number of variables encountered in practice, an attempt to study any one reaction or relation being affected by other reactions the relative importance of which cannot be estimated.

The factors that affect the extent of removal of sulfur in the basic open-hearth process are generally considered to be:

1. Basicity of the slag: (*a*) Iron oxides in the slag; (*b*) carbon in the metal or carbide in the slag; (*c*) temperature. These factors affect the reactions:

$$FeS + CaO = CaS + FeO$$
$$FeS + CaO + C = CaS + CO + Fe.$$

2. Amount of sulfur in the gas.
3. Amount of manganese in the metal.

The factors which affect the rate of removal of sulfur include, in addition to these:

4. Fluidity of the slag: (*a*) Normal changes in fluidity with temperature; (*b*) changes in fluidity because of the addition of special reagents such as fluorspar.
5. Agitation of the bath.

Within the past two years, two papers have been presented dealing with the influence of sulfur in the gas on slag and metal. Nead[1] has shown that if a gas high in sulfur be used for heating, the metal and slag will absorb sulfur. Whitely[2] concluded from his experiments that if a

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† Massachusetts Institute of Technology Theses, 1923–24.

[1] Absorption of Sulfur from Producer Gas in Open-hearth Furnaces. *Trans.* (1924) **70**, 176.

[2] J. West Scot: *Proc.* Iron and Steel Inst. (1923).

sulfur-free gas is used, a slow but steady decrease in sulfur in the metal will occur in the acid open-hearth process. Developments of the last three years in the field of absorption of gases by aqueous solutions have led the author to believe that sulfur absorption and desulfurization in the basic open-hearth furnace can be predicted quantitatively. To this end experiments have been carried out covering the following subjects:

1. The distribution ratio of sulfur between gas and slag (*a*) iron oxides formed on melting, (*b*) slags containing lime.

2. Rates of absorption of sulfur by slags from gases high in sulfur, and rates of desulfurization of slags by gases free from sulfur.

Experimental Furnaces

A small tilting furnace, constructed of magnesite brick and fired with illuminating gas and oxygen-enriched air was used to study the distribution ratio of sulfur between gas and slag, and the rate of absorption of sulfur by slags from gases high in sulfur. This furnace had a capacity of 1 to 4 lb. of material. The sulfur content of the gas was regulated by adding pure SO_2 to the illuminating gas, thus giving in the furnace conditions comparable to commercial practice, the hydrogen sulfide in producer gas or coke oven gas being burnt to sulfur dioxide in the open-hearth furnace.

$$2H_2S + 3O_2 = 2SO_2 + 2H_2O$$

A synthetic slag, free from sulfur, composed of about 40 per cent. FeO, 30 per cent. CaO, and 30 per cent. SiO_2 was melted in this furnace and allowed to react with the gas until equilibrium between gas and slag had been reached.

A Booth two-electrode furnace *B* of 100 lb. capacity was used to study the rate of desulfurization of slags. Air leakage into the furnace supplied an atmosphere initially free from sulfur. This furnace was charged with boiler punchings and a slag made with pure lime and pure silica sand. Experiments on commercial furnaces were made in the furnaces of the Lackawanna plant of the Bethlehem Steel Co. The furnaces are standard stationary open hearths of 100 tons capacity, fired with producer gas. In the text, the experiments on these furnaces will be designated by heat numbers.

In all furnaces, the sulfur content of the waste gas was determined by drawing a sample of the gas through iodine and precipitating the sulfuric acid formed with barium hydroxide.

Results

Distribution Ratio between Gas and Slag

Iron Oxide Formed on Melting.—Two heats were studied in the 100-ton furnace to ascertain the amount of sulfur picked up or lost by the scrap on melting down. Samples of oxide drippings from the scrap were taken

after the scrap had begun to "sweat" and at the same time the exit gases were analyzed for sulfur. In one of the two heats, a sample of the scrap itself was obtained from a "mushroom" that grew out on one of the pieces. The scrap charge in these two heats was all rail scrap—ends, blooms, and butts. The results are as follows:

Heat Number	17-244[3]	26-P-380
Sulfur in scrap, per cent	0.033	0.037
Sulfur in oxide drippings, per cent	0.074	0.054
Sulfur in mushroom, per cent	0.075	
Sulfur dioxide in gas over bath, volume per cent	0.069	0.045
Sulfur dioxide in exit gas, volume per cent		0.027
Ratio, $\frac{\text{vol. per cent. sulfur dioxide in gas over bath}}{\text{per cent. sulfur in oxide drippings}}$	0.93	0.84

The concentration of sulfur over the bath in heat 26-P-380 has been taken as the concentration found during periods in the heat when little or no sulfur was being picked up or lost by the slag. This averaged 0.045 per cent. SO_2. The exit gases during melting contained only 0.027 per cent. SO_2, showing that a large amount of sulfur was being lost by the gas, corresponding to a rise from 0.037 per cent. to 0.054 per cent. sulfur in the scrap.

It will be noted that the ratio of sulfur in the gas to sulfur in the drippings has nearly the same value for both heats. Further the scrap mushroom had the same analysis as the drippings in the first heat, indicating that the reduction of SO_2 to FeS will go to the same extent whether the sulfur enters iron oxide or metallic iron. The chemical reaction in this case is the reduction of SO_2 by iron, the reaction being reversible:

$$SO_2 + 2Fe = FeS + FeO$$

or

$$3SO_2 + 7Fe = 3FeS + 2Fe_2O_3$$

or both. In either case, the sulfur in the slag is proportional to the sulfur in the gas, the iron being saturated with iron oxide during this period. The conclusion may be drawn from these results that if a gas entirely free from sulfur were used during the melting, any iron in direct contact with the gases would be completely, or nearly completely, desulfurized before it reached the bath proper. An investigation of this phase of the subject is being undertaken to determine at what point in the furnace most of the pick-up occurs, *i. e.*, whether the end at which the gas enters is most active in sulfur absorption or whether the pick-up is general all over the bath The speed with which the scrap picks up sulfur is also being studied.

Slags Containing CaO.—The following table shows the values of the distribution ratios in the gas-fired experimental furnace *A*, and in the open-hearth furnaces *C*.

[3] J. L. Keats: Massachusetts Institute of Technology, Doctor's Thesis, 1924.

	Per Cent. Sulfur in Slag 1	Volume Per Cent. Sulfur Dioxide in Waste Gas 2	Distribution Ratio $\frac{2}{1}$
Experimental furnace *A*			
Run No. 1	0.037	0.00926	0.250
Run No. 2	0.016	0.00403	0.252
Run No. 3	0.045	0.0120	0.267
Open-hearth furnaces *C*			
Heat 17244	0.255	0.0695	0.272
Heat 26-P-347	0.148	0.0434	0.293
Heat 29-P-325	0.116	0.0276	0.238
Heat 26-P-380	0.0668	0.0170	0.254

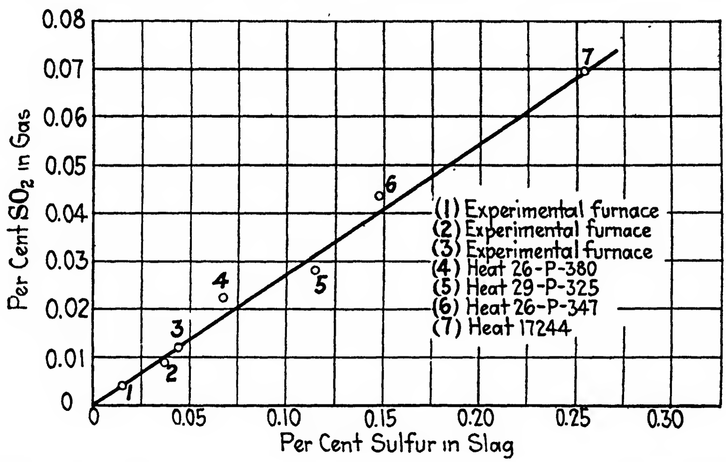

Fig. 1.—Per cent. sulfur dioxide in gas versus per cent. sulfur in slag.

These results are shown in Fig. 1, from which per cent. sulfur in slag = 3.7 × per cent. sulfur dioxide in gas. The analyses of these slags are as follows:

	Per Cent. S	Per Cent. SiO_2	Per Cent. FeO	Per Cent. MnO	Per Cent. CaO	Per Cent. MgO
Experimental furnace *A*						
Run No. 1	0.037	19.7	57.2	0.0	19.7	3.4
Run No. 2	0.016	11.8	74.3	0.0	11.8	2.1
Run No. 3	0.045			not analyzed		
Open-hearth furnaces *C*						
Heat 17244	0.255	19.46	6.9	16.45	40.50	3.65
Heat 26-P-347	0.148	27.70	38.88	14.80		
Heat 29-P-325	0.116	10.02	33.55	5.80		
Heat 26-P-380	0.0668	24.76	29.55	13.60		

In the experimental furnace *A*, the sulfur in the slag was present as iron, calcium, or magnesium sulfides, the relative amounts of each being unknown. All the slags from the open-hearth furnaces *C* contained considerable amounts of manganese oxide and in these cases there could be present, in addition to the sulfides mentioned, manganese sulfide. However, the distribution ratio between gas and slag is essentially constant for all the heats, which leads to the conclusion that either all the

sulfides have the same distribution ratio with the gas or that one of the sulfides, iron, calcium or magnesium, predominates in all the slags. In view of the facts that lime is so much stronger as a base than iron oxide and that the magnesium oxide is so low in all the slags, it seems that the sulfur in the slag must be present almost entirely as calcium sulfide.

The reaction by which SO_2 is reduced to CaS in the slag is not known but experimental work is being planned to study this phase of the subject.

The reactions under consideration are:

$$SO_2 + 3CO + CaO = CaS + 3CO_2$$
$$SO_2 + CaO + 3Fe = CaS + 3FeO$$

The slag in an open-hearth furnace is saturated with carbon monoxide and carbon dioxide and also with iron vapor. Either carbon monoxide or iron vapor will reduce sulfur dioxide and, in the presence of lime, the reduced sulfur dioxide would form calcium sulfide, the principal sulfide in the slag.

It is evident from these results that the sulfur content of the slag will have a value directly proportional to the concentration of sulfur in the gas, provided that sufficient time is allowed for the reaction to reach equilibrium. In practice, a constant per cent. of sulfur in the slag is not always reached because of changes in slag weight, interchange of sulfur between metal and slag, and insufficient time for equilibrium to be reached. However, until equilibrium is established, the slag is always losing or absorbing sulfur to or from the gas, depending on the sulfur concentrations in the slag and gas.

A run was made in the Booth electric furnace *B*, with a charge consisting of 75 lb. of boiler punchings and a pure calcium silicate slag. The concentration of sulfur in the gas was controlled by adding sulfur dioxide to a small amount of illuminating gas, using a special burner inserted in the tap hole of the furnace. The amount of sulfur in the gas was gradually increased throughout the run and the slag and metal showed the following analyses over a 2½-hr. period:

	Per Cent.
Sulfur in slag when melted	0.036
Sulfur in slag at end	0.121
Sulfur in metal when melted	0.052
Sulfur in metal at end	0.099

The final concentration of sulfur in the gas was not determined on account of loss of the gas sample. This run showed, however, that by increasing the sulfur content of the gas, the metal and slag picked up a large amount of sulfur.

Rates of Absorption and Desulfurization

Let us take a definite concentration of sulfur in the gas, such that the per cent. in the slag must be 0.15 so as to satisfy the distribution ratio just

given. If this gas is in contact with two slags A and B, A containing 0.10 per cent. sulfur and B 0.20 per cent., slag A will pick up sulfur and slag B will lose it. The rate of absorption or desulfurization is proportional to the distance from equilibrium,[4] therefore, slag A (which is 0.05 per cent. below equilibrium) will absorb sulfur at the same rate that slag B (which is 0.05 per cent. above equilibrium) loses it. The distance from equilibrium may be called the "driving force" for the reaction; and for cases where the slag is picking up sulfur it may be expressed as $(S_e - S)$ where S_e is the per cent. sulfur in equilibrium with the gas and S is the actual per cent. of sulfur in the slag. For slag A, the driving force is $(0.15 - 0.10) = 0.05$ per cent. sulfur. Conversely for slags losing sulfur the driving force is $(S - S_e)$, which for slag B is $(0.20 - 0.15) = 0.05$ per cent.

If a liquid is absorbing a gas under given conditions and the area of the liquid is suddenly doubled, the rate of absorption will also be doubled as twice as much liquid comes into contact with the gas. The rate of absorption is, therefore, directly proportional to the driving force and to the area that is effective for absorbing. Adopting the formulation of Whitman and Keats,[5] this may be expressed mathematically as:

$$\frac{dS}{d\theta} = KA(S_e - S)_{ave}$$

(1) for absorption of sulfur;

$$-\frac{dS}{d\theta} = KA(S - S_e)_{ave}$$

(2) for loss of sulfur or desulfurization.

$\frac{dS}{d\theta}$ = amount of sulfur absorbed by slag per unit of time

$-\frac{dS}{d\theta}$ = amount of sulfur lost by slag per unit of time.

A = area of reacting surface;

S_e = sulfur concentration in equilibrium with gas;

S = sulfur concentration at any time θ;

$(S_e - S)$ = driving force for sulfur absorption;

$(S - S_e)$ = driving force for desulfurization;

K = absorption coefficient.

Equation (1) may be integrated to give:

$$K = \frac{2.3 \log \frac{(S_e - S_o)}{(S_e - S)}}{A\theta}$$

(2.3 = conversion from natural to common logarithms.)

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[4] W. K. Lewis: Principles of Counter-current Extraction. *Ind. & Eng. Chem.* (1916) **8**, 827.

[5] W. G. Whitman and J. L. Keats: Rates of Absorption and Heat Transfer between Gases and Liquids. *Ind. & Eng. Chem.* (1922) **14**, 186.

K will be expressed as per cent. sulfur absorbed per unit of time per per cent. driving force per square foot of reacting surface, when the sulfur concentrations are expressed as per cent. To obtain K as pounds of sulfur, it is only necessary to divide the value found by the equation above by 100 and multiply by the pounds of slag under consideration.

Physical Concept of Sulfur Absorption or Loss

In transferring any material from a gas to a liquid or solid, or vice versa, the major resistance to the transfer is found at the boundary separating the two.[6] This resistance is composed of a gas film and a liquid film,[7] in certain cases one of these films being controlling. In the

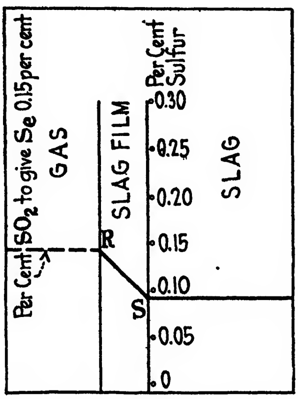

FIG. 2.—SULFUR ABSORPTION.

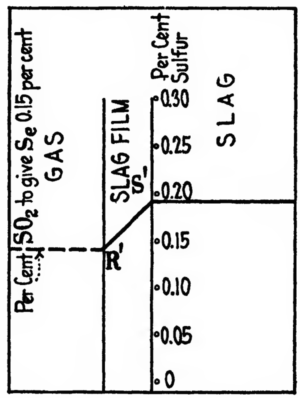

FIG. 3.—DESULFURIZATION.

absorption of benzol from coke-oven gas by straw oil, the major resistance is the viscous surface film on the straw oil through which the benzol must pass before entering the main body of the oil. In the open hearth, the flow of sulfur from gas to slag, or vice versa, may be considered in the same light; namely, the sulfur must pass from the gas through a slag film before entering the main body of the slag. This is represented diagrammatically in Fig. 2 for absorption of sulfur and in Fig. 3 for desulfurization. For the two conditions given on page 6, Fig. 2 applies to slag A and Fig. 3 to slag B. The points R and R' represent the sulfur in equilibrium with the gas, while S and S' are the concentrations in the slag, 0.10 and 0.20 per cent. for slags A and B respectively.

In the equation $\frac{dS}{d\theta} = KA(S_e - S)$, K, the absorption coefficient, is given in terms of amount of sulfur absorbed in 1 min. through 1 sq. ft. of

[6] Walker, Lewis and McAdams: "Principles of Chemical Engineering." Chap. 2. McGraw-Hill Book Co., N. Y., 1923.

[7] W. G. Whitman: Two Film Theory of Gas Absorption. *Chem. & Met. Eng.* (1923) **29** 146.

surface area when there is a difference of 1 per cent. between the equilibrium and the actual sulfur contents.

Inasmuch as the slag film controls this rate, conditions affecting its characteristics will affect the numerical values of K. These conditions are: Fluidity of slag, agitation of bath, gas velocity over bath.

Fluidity.—As the slag becomes more and more viscous, the flow of material into it, other things being constant, will necessarily slow up.[8] Conversely, a fluid slag will allow material to enter it more rapidly than will a viscous slag. As the fluidity increases, the numerical value of the absorption coefficient should increase. Temperature affects the value of the coefficient inasmuch as increased temperature means higher fluidity.

Agitation.—Agitation serves two purposes as regards absorption. It increases the effective area for reaction and it may break up the slag film and allow the body of the slag to come into contact with the gas.[9] Increased agitation should, therefore, increase the absorption coefficient.

Gas Velocity.—Gas velocity affects the slag film in the same manner as agitation. If the gas velocity is high enough, the slag may be agitated in the same manner as a high wind causing surface agitation on a body of water. This effect was noticed particularly in one of the experimental heats where, with no metal present to give agitation by carbon removal, the slag was agitated considerably by running the gas velocity very high. When both films are factors, the influence of gas velocity on the liquid film is very slight.[10]

Experimental Results for Rate of Absorption

The gas-fired furnace was charged with slag containing 0.016 per cent. sulfur, and the slag held molten for 35 min. Samples of slag taken at intervals of about 10 min. and analyzed for sulfur showed:

Sample	Time from Start, Minutes	Per Cent. Sulfur
0	0	0.016
1	11.5	0.036
2	20.5	0.0412
3	35.0	0.044

The area of the slag-metal surface in this furnace was 0.314 sq. ft. and 1 lb. of slag was charged in the furnace. The equilibrium per cent. sulfur was 0.045.

From these data, the value of $K = 0.00323$ lb. of sulfur per min. per sq. ft. slag-gas surface per per cent. driving force.

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[8] R. T. Haslam, R. L. Hershey, and R. H. Kean: The Mechanism of Absorption. *Ind. & Eng. Chem.* (1924), **16**.

[9] W. G. Whitman and D. S. Davis: Comparative Absorption Rates for Various Gases, presented before the Ithaca meeting of the Am. Chem. Soc., Sept., 1924.

[10] R. T. Haslam, W. P. Ryan and H. C. Weber: Some Factors Influencing the Design of Absorption Apparatus. *Trans.* Am. Inst. of Chem. Eng. (1923) **15**, 177.

Data obtained on heat 26-P-380, Bethlehem Steel Co., Lackawanna plant, give for the last hour and twenty minutes of working a coefficient of 0.0045 lb. of sulfur absorbed per minute per square foot of gas-slag surface per per cent. driving force. During this period, the bath was working steadily from a hot metal addition. The data collected over this period are:

Time	Per Cent. Sulfur in Metal	Per Cent. Sulfur in Slag	Weight of Slag, Pounds	Per Cent. Sulfur Dioxide in Gas	Pounds Sulfur in Furnace	Increase in Pounds Sulfur
7:46	0.0250	0.1212	30,500	0.0475	93.0	
9:06	0.0253	0.1216	35,500		102.6	9.6

The slag weight was calculated by a manganese balance from the following data:

Time	Weight Metal, Pounds	Pounds Manganese in Furnace	Per Cent. Manganese in Metal	Per Cent. Manganese in Slag
7:46	229,000	2145	0.183	5.68
9:06	235,000	2230	0.174	5.13

The 6000 lb. of hot metal added at 8:09 contained 0.0385 per cent. sulfur = 2.3 lb. The total amount of sulfur picked up from the gas was 9.6 − 2.3 = 7.3 lb.

From Fig. 1, a gas containing 0.0475 per cent. sulfur dioxide is in equilibrium with a slag containing 0.175 per cent. sulfur. The average driving force over this period was therefore 0.175 − the average per cent. sulfur in the slag, which was 0.1297 = 0.0453. The total pounds of sulfur picked up from the gas was 7.3, the time was 80 min., and the gas-slag area of the furnace, 450 sq. ft.

$$K = \frac{S}{\theta \times A \times (S_e - S)} = \frac{7.3}{80 \times 450 \times 0.0453} = 0.0045$$

When the heat was ored, the heat melted with 0.85 per cent. carbon, a very violent reaction took place and the gas was shut off for about 5 min. During this period, the slag was in contact with a sulfur-free atmosphere and lost 11.2 lb. of sulfur in 22 min. The analyses were:

Time	Per Cent. Sulfur in Metal	Per Cent. Sulfur in Slag	Slag Weight,[a] Pounds	Pounds of Sulfur in Furnace
6:23	0.0347	0.1964	23,250	123.7
6:45	0.0392	0.0880	25,600	112.5

[a] Calculated from manganese balance on slag and metal.

Time	Weight Metal, Pounds	Pounds Manganese in Furnace	Per Cent. Manganese in Metal	Per Cent. Manganese in Slag
6:23	226,000	2145	0.459	4.82
6:45	229,000	2145	0.181	6.53

The coefficient of desulfurization could not be obtained as the furnace was on air only part of this period. The desulfurization was undoubtedly due to the sulfur-free atmosphere during a part of the ore boil.

No data have been found in the literature where the sulfur concentration in the gas and slag are given simultaneously. However, knowing the sulfur content of the coal used in heating a given furnace and the gas analysis of the products of combustion and the ash analysis, the sulfur concentration may be calculated. This has been done for the following heats, except that of Peterson[11] in which the per cent. of sulfur in the slag rose regularly enough to estimate the equilibrium per cent. sulfur.

Source of Data	Conditions	K
Keats[12]	First ore addition, violent boil	0.0039
Keats	Third ore addition, fair boil	0.0045
Peterson	No ore added, per cent. carbon 0.38 down	0.0040
Kinney & McDermott[13]	No ore added, per cent. carbon 0.31 down	0.0035

The analyses of slag and metal for sulfur in these runs is as follows:

	Per Cent. Sulfur in Slag		Per Cent. Sulfur in Metal	
	Beginning	End	Beginning	End
Keats, first ore addition	0.047	0.055	0.0295	0.0346
Keats, third ore addition	0.063	0.113	0.0291	0.0283
Peterson	0.110	0.316	0.100	0.077
Kinney and McDermott	0.14	0.22	0.038	0.038

The experimental run given above (page 519), with no agitation from carbon but with very high gas velocity gave $K = 0.00323$.

The method of calculating K in this experiment is as follows:

For sample No. 1, θ, 11.5 min.; S_e, 0.045 per cent. sulfur; S_o, 0.016 per cent. sulfur; S, 0.036 per cent. sulfur; A, 0.314 sq. ft. From the integrated equation on sulfur absorption.

$$K = \frac{2.3 \log \dfrac{(S_e - S_o)}{(S_e - S)}}{A\theta} = \frac{2.3 \times 0.508}{0.314 \times 11.5} = 0.323 \text{ per cent. sulfur per min.}$$

per sq. ft. per per cent. driving force.

To reduce this to pounds of sulfur, we must divide by 100 and multiply by the pounds of slag

$$K = \frac{0.323 \times 1}{100} = 0.00323 \text{ lb. sulfur per min. per sq. ft. reacting surface}$$

per per cent. driving force.

[11] *Rev. Metal. Mem.* (1910) 198.

[12] *Loc. cit.*

[13] *Proc.* Am. Iron and Steel Inst. Oct., 1922.

The equation may also be used in the differential form as follows, expressing $\frac{dS}{d\theta}$ as pounds of sulfur per unit of time.

$$dS = (0.00036 - 0.00016) = 0.00020 \text{ lb. sulfur}$$
$$d\theta = 11.5 \text{ min.}$$
$$S_e = 0.045 \text{ per cent.}$$
$$S_o = 0.016 \text{ per cent.}$$
$$S = 0.036 \text{ per cent.}$$
$$A = 0.314 \text{ per cent.}$$
$$\frac{dS}{d\theta} = KA\,(S_e - S)_{ave}$$
$$(S_e - S)_1 = S_e - S_o = 0.029$$
$$(S_e - S)_2 = S_e - S = 0.009$$

Logarithmic average of 0.029 and 0.009 = 0.0171

$$K = \frac{0.00020}{11.5 \times 0.314 \times 0.0171} = 0.00323 \text{ lb. sulfur per min. per sq. ft. area}$$
per per cent. driving force.

Results for Rate of Desulfurization

The two runs for desulfurization in the Booth electric furnace B were made by melting down boiler punchings, making a slag with lime and silica, and adding enough iron sulfide to give about 0.5 per cent. sulfur in both slag and metal. As previously stated, air leakage into the furnace supplied an atmosphere initially free from sulfur. The essential data collected for these two runs are:

	Run No. 1	Run No. 2a	Run No. 2b
Per cent. sulfur in slag at start	0.451	0.424	0.181
Per cent. sulfur in slag at end	0.160	0.321	0.166
Per cent. sulfur in metal at start	0.843	0.372	0.378
Per cent sulfur in metal at end	0.733	0.335	0.318
Vol. per cent. sulfur dioxide in gas	0.030	0.050	0.009
Equilibrium per cent. sulfur in slag (from Fig. 1)	0.112	0.185	0.033
Total pounds sulfur removed from slag to gas	0.0261	0.0230	0.0240
Time of run, minutes	120	81	60
Slag-gas area, square feet	0.763	0.763	0.763
Gas velocity	very low for all three		
K	0.00193	0.00194	0.00372

The slag analyses for these runs (2a and 2b same heat) are:

	Run No. 1	Runs No. 2a and 2b
SiO_2	39.06	23.96
FeO	14.2	28.4
Fe_2O_3	2.49	3.62
CaO	13.5	22.30
MgO	22.8	13.10
MnO	1.21	1.66

The constants agree with those found for sulfurization inasmuch as the percentage of carbon was very low in these heats, never getting above 0.10 in spite of numerous additions of pig iron. There was, therefore, practically no agitation except at the time of adding the pig iron. The reaction of the pig with the iron oxides in the slag usually lasted from 1 to 2 min.; and as samples were taken at 15-min. intervals, adding 1 to 2 lb. of pig after each sample, there was agitation for not more than 10 to 15 per cent. of the time. The slag, however, was extremely fluid. Combining these with the results of sulfurization, we have for the absorption coefficient K:

Run No.	K	Condition	Furnace
1	0.0045	Pig addition, good agitation	C
2	0.0045	Ore addition, fair agitation	C
3	0.0040	No ore added, per cent. carbon, 0.38 down	C
4	0.0039	Ore addition, violent agitation	C
5	0.0037	Electric furnace, carbon below 0.10 per cent	B
6	0.0035	No ore added, per cent. carbon, 0.31 down	C
7	0.0032	Slag only, agitation from high gas velocity	A
8	0.0019	Electric furnace, carbon below 0.10 per cent	B
9	0.0019	Electric furnace, carbon below 0.10 per cent	B
			C

The effect of agitation is, therefore, to increase the coefficient somewhat, agitation by high gas velocity apparently having an important effect, as shown by Run No. 7. The effect of fluidity could not be studied, except that it may be here noted that the experimental runs in the Booth furnace, B, were at a higher temperature than is usually carried in the open hearth. The temperatures in these runs were close to 1650° to 1700° C. (3002° to 3092° F.). This would tend to make the slags more fluid than normal open-hearth slags and to increase the coefficient. It is highly probable that this increased fluidity due to higher temperatures somewhat balanced the lack of agitation in the electric-furnace runs.

It has been shown that the rate at which a slag will lose sulfur to a low-sulfur gas is the same as the rate at which a slag will pick up sulfur from a high-sulfur gas, under comparable conditions, the equations for these rates being given in the discussion of the theory of absorption and desulfurization. The results just given show that for normal open-hearth practice the rate of sulfur absorption is about 0.004 lb. of sulfur per minute, per square foot of slag-gas surface, per per cent. driving force or distance from equilibrium. The same coefficient will hold when desulfurization of the slag is occurring. A lower rate of desulfurization is to be expected in the electric furnace if the carbon is very low.

Applications

In considering the application of the experimental results to practical operation it is necessary to consider two points: (1) how much sulfur may

be removed from the bath in the usual time of working a heat by a fuel gas free from sulfur; (2) will the savings obtained by desulfurizing the bath with a clean gas be offset by the cost of cleaning the gas and by any other disadvantages incurred.

The first question to be considered is obviously how much sulfur can be removed with a gas free from sulfur. The following conditions will be specified for the purpose of calculating the amount of sulfur removed:

1.—Gas almost completely cleaned of sulfur
2.—0.020 per cent. sulfur in finished steel
3.—0.10 per cent. sulfur in slag at end
4.—100 ton stationary furnace
5.—220,000 lb. steel
6.—28,000 lb. slag
7.—Time of heat 8 hr., end of charging scrap to tap.
8.—The gas will be desulfurizing the slag at all times.
9.—Consider, therefore, that the slag averages 0.10 per cent. sulfur throughout.

Total sulfur at end is $220{,}000 \times 0.00020 =$	44 lb.
$28{,}000 \times 0.00100 =$	28 lb.
	72 lb.

The equation for desulfurization is

Pounds of sulfur removed $= KA\theta\,(S - S_e)$

$S - S_e =$	0.10 per cent.
$A =$	450 sq. ft.
$K =$	0.004
$\theta =$	$8 \times 60 = 480$
Sulfur removed by the gas is $0.10 \times 450 \times 0.004 \times 480 =$	86.3 lb.

Let the charge consist of 50 per cent. scrap and 50 per cent. hot metal with the scrap averaging 0.040 per cent. sulfur and a total charge of 230,000 lb.

Total sulfur in charge = pounds sulfur at end + pounds sulfur removed $= 72 + 86.3 =$	158.3 lb.
Scrap contains $115{,}000 \times 0.0004 =$	46.0 lb.
Hot metal can contain	112.3 lb. = 0.097 per cent. sulfur

Let charge consist of 25 per cent. scrap and 75 per cent. hot metal:

Total sulfur in charge = 158.3 lb.
Scrap $57{,}000 \times 0.004 =$ 23.0 lb.

Hot metal can contain 135.3 lb. = 0.078 per cent. sulfur

We may then say that any charge containing 75 per cent. hot metal or under can be made with hot metal containing from 0.08 per cent. sulfur up, depending on the percentage of hot metal in the charge.

Data on heats 17244[14] and 26-P-380 show that the rate at which sulfur may be removed from the metal by the slag under favorable slag conditions, *i. e.*, fairly low sulfur (0.08 to 0.16 per cent.), with 35 to 45 per cent. CaO, and with good action on the bath, is at a rate of from 12 to 33 lb. per hr.

Heat number	17244	26-P-380
Time	5:34–7:52	6:45–8:00
Per cent. sulfur in metal	0.0342–0.0228	0.0392–0.0220
Drop in per cent. sulfur	0.0114	0.0172
Time, in hours	2.3	1.25
Drop in per cent. sulfur per hour	0.0050	0.0138
Sulfur removed per hour, pounds	12.0	33.0

The rate at which sulfur must be removed from the metal to satisfy the conditions set up in the calculation is $158.3 - 44 = 114.3$ lb. in 8 hr., an average of 14.2 lb. per hr. This falls just within the range just given, and with low-sulfur slags this should insure desulfurization of the metal to the specified content in the time allotted.

The second question involves a consideration of the advantages and disadvantages resulting from the use of clean gas. Listing the advantages of the clean gas process we would have—

Avoidance of high-sulfur heats encountered in present practice with gases such as producer gas of medium-sulfur content and with uncleaned coke-oven gas of high-sulfur content.

Use of high-sulfur metal from the blast furnace with the saving at the blast furnace from: (*a*) increased capacity, (*b*) lower coke consumption, (*c*) lower limestone consumption.

Lower limestone consumption in the open hearth from lower silicon pig iron resulting from its high-sulfur content.

Cleaner regenerators in the open hearth from tar and soot free producer gas.

Steam in producer gas removed by scrubbing; drop from about 10 to about 3.2 per cent. H_2O (saturation at 25° C. on dry gas basis).

Against these advantages must be placed the following:

The cost of cleaning the gas.

Loss of sensible heat in producer gas.

Loss of tar in producer gas.

The net saving by using clean gas may be calculated by itemizing the savings and losses on the foregoing items. In calculating this, a comparison must be made between current practice and that which could be

[14] Keats: *Loc. cit.*

used with clean gas. For this purpose the following conditions are set for current practice.

Blast-furnace hot metal: per cent. sulfur, 0.030 average; per cent. silicon, 1.25 average.

100-ton open-hearth charging 50 per cent. hot metal and 50 per cent. scrap.

As shown, completely cleaned gas will allow at least 0.080 per cent. sulfur, if not higher, in a charge of 50 per cent. hot metal and 50 per cent. scrap. With these specifications in mind the savings on the items listed under advantages are:

Saving on Time for Heats Held in Furnace on Account of High Sulfur.—The cost of producing steel in the open hearth has been taken at $7 per ton. The time lost against the savings effected in eliminating this time is given below.

Time Lost, Hours per Month per Furnace	Savings, Dollars per Ton	Savings, Dollars per Month per Furnace
0	0.000	0
1	0.010	60
2	0.020	120
5	0.049	294
10	0.098	588
15	0.146	875
20	0.195	1180

Savings at Blast Furnace.—

Increase in furnace capacity	$0.040
Decrease in coke consumption	0.137
Decrease in limestone consumption	0.008
Total	$0.185 per ton of steel

Saving in Limestone in Open Hearth.—The decreased silicon in high-sulfur pig iron has been estimated in terms of limestone saved at the open hearth at $0.038 per ton of steel.

Cleaner Regenerators.—Indeterminate.

Saving in Reducing Water Content of Producer Gas from 10 *Per Cent. to* 3.2 *Per Cent.* (*Saturation at* 25° *C.*).—This has been estimated at $0.022 per ton of steel.

Cost of Cleaning the Gas.—A very economical method of removing hydrogen sulfide from gas is scrubbing with a dilute solution of soda ash, the spent liquor from the absorption being revivified by aeration. This system[15] is in use in thirty gas plants and in one steel plant. At the steel plant, the H_2S in coke-oven gas is lowered from about 500 gr. per 100 cu. ft. to about 100 gr. per 100 cu. ft., a removal of about 80 per cent. This

[15] F. W. Sperr, Jr.: The Absorption of Hydrogen Sulfide. Presented at Ithaca meeting of Am. Chem. Soc., Sept., 1924.

concentration is too high to remove a large amount of sulfur in the open hearth but is low enough to insure little or no trouble through high-sulfur heats, and gives a waste gas lower in sulfur than producer gas from coal containing 1.0 per cent. sulfur. The writer understands that the cost of reducing the sulfur from 500 to 50 gr. per 100 cu. ft. by this process, including fixed charges, is about 0.50 cents per 1000 cu. ft. of gas. Complete purification costs about twice as much. Producer gas from 1.0 to 1.2 per cent. sulfur coal contains approximately 100 gr. of sulfur per 100 cu. ft. To reduce this to 10 gr. would cost 0.40 cents per 1000 cu. ft. and to cool the gas before scrubbing would cost another 0.40 cents, a total cost of purifying producer gas of 0.80 cents per 1000 cu. ft. On the basis of one ton of steel the cost would be:

Coke-oven gas	$0.13
Producer gas	0.32

Sensible Heat Loss in Producer Gas.—The total sensible heat lost cannot be charged against the first five items, for when heating cold gas much greater differences in temperature between gas and checker hold than when gas at 1100° F. is preheated to 2200° F. Further the gas regenerators will be cleaner, thus increasing the heat transfer. The net loss of sensible heat has been estimated at $0.036 per ton of steel.

Loss of Tar from Producer Gas.—The loss of tar would remove a small amount of latent heat from the gas, but this is considered balanced by the greater cleanliness of the regenerators and by the fact that all the tar may be recovered in scrubbing.

The items which may be placed against each other to determine the practicability of completely removing the sulfur from coke oven or producer gas are:

Item	Savings, Dollars per Ton of Steel		Cost, Dollars per Ton of Steel	
	Coke-oven Gas	Producer Gas	Coke-oven Gas	Producer Gas
Time lost at present due to high-sulfur heats	Same for both, varies with time lost			
Use of 0.08 per cent. sulfur in hot metal instead of 0.03 per cent. sulfur	0.185	0.185		
Lower limestone consumption in open hearth	0.038	0.038		
Clean regenerators	None	Indeterminate		
Removal of steam from gas	None	0.022		
Cost of cleaning gas			0.13	0.320
Loss of sensible heat in fuel gas			None	0.036
Loss of tar in scrubbing			None	Indeterminate

The saving in cleaning each gas, omitting at this point the saving of time lost through high-sulfur heats and the cost of cleaning the gas, will be: Coke-oven gas, $0.223 per ton of steel; producer gas, $0.209 per ton of steel.

The net saving in dollars per ton of steel will be:

For coke-oven gas, elimination of time lost through high-sulfur heats, +0.223 − 0.130.

For producer gas, elimination of time lost through high-sulfur heats, +0.209 − 0.320.

The net saving for each gas is as follows:

Time Lost, Hours per Month per Furnace	Net Saving, Dollars per Ton Coke-oven Gas	Producer Gas
0	+0.093	−0.111
1	+0.103	−0.101
2	+0.112	−0.092
5	+0.142	−0.062
10	+0.191	−0.013
15	+0.239	+0.035
20	+0.288	+0.084

The net saving per furnace per month for the conditions shown above are:

Time Lost, Hours per Furnace per Month	Net Saving, Dollars per Furnace per Month Coke-oven Gas	Producer Gas
0	560	−670
1	620	−610
2	670	−550
5	850	−370
10	1150	− 80
15	1430	210
20	1730	500

Completely removing the sulfur from coke-oven gas, and using this alone as a fuel, would be profitable even if no time were lost due to sulfur under present operating conditions. The use of clean producer gas would be unprofitable, unless an excessive amount of time is at present lost from charges high in sulfur or from the use of a high-sulfur coal.

Two other methods of operation must be considered at this point: (1) The use of coke-oven gas and tar; (2) the use of partly cleaned coke-oven gas, insuring no time lost on account of high-sulfur heats but at the same time necessitating the use of a low-sulfur pig iron in the charge.

Use of Coke-oven Gas and Tar

The relative amounts of these two fuels, when used together, vary considerably. Any combination of the two giving not more than 0.035 per cent. sulfur dioxide in the products of combustion will prevent the

slag and metal from picking up sulfur from the gas when charges of hot metal and scrap averaging 0.030 to 0.045 per cent. sulfur are used. Tar of the composition 93.5 per cent. carbon, 6.0 per cent. hydrogen, and 0.5 per cent. sulfur, when burned with theoretical air, gives 1720 cu. ft. of waste gas (at 32° F. and 760 mm.) per gallon. Coke-oven gas of 540 B. t. u. per cu. ft. when burned under the same conditions gives 5.6 cu. ft. of waste gas per cubic foot. To obtain a waste gas containing 0.035 per cent. sulfur dioxide, it is necessary to take into account only the sulfur content of the fuels and the changes in volume on combustion. Tar containing 0.5 per cent. sulfur gives a waste gas containing 0.0326 per cent. sulfur dioxide, and coke-oven gas containing 500 gr. of sulfur per 100 cu. ft. gives 0.134 per cent. sulfur dioxide in the waste gas. The amount of sulfur dioxide in waste gas from any amount of sulfur in the coke-oven gas will be in the same ratio as the values given above; *i. e.*, to obtain the sulfur dioxide in the waste gas, the grains of sulfur per 100 cu. ft. of coke-oven gas are multiplied by 0.000268.

Using 7,000,000 B. t. u. as the heat required to produce 1 ton of steel, and 0.035 per cent sulfur dioxide as the safe limit for sulfur in the waste gas, the following table has been derived. The relative amounts of coke-oven gas and tar required to melt 1 ton of steel are listed with changing amounts of sulfur in the coke-oven gas. If coke-oven gas is purified to 131 gr. of sulfur per 100 cu. ft., the waste gas will contain 0.035 per cent. sulfur dioxide, and under these conditions any ratio of gas and tar may be used.

Grains of Sulfur in 100 Cu. Ft. of Coke-oven Gas	Combination to Give 0.035 Per Cent. Sulfur Dioxide in Waste Gas	
	Gallons of Tar	Cubic Feet of Coke-oven Gas
500	42.7	335
400	42.4	410
300	41.6	670
200	38.9	1,500
150	29.6	4,300
145	27.6	5,270
140	21.5	6,830
135	12.8	9,600

Any amount of tar over that here given for a given sulfur concentration in the coke-oven gas will give a waste gas lower than 0.035 per cent. sulfur dioxide, as will an excess of air for combustion. At 135 gr. per 100 cu. ft., the gas and tar are being burned very nearly in the proportion in which they are produced. With gas cleaned below 130 gr., tar may be saved by burning a combination higher in gas.

The use of completely purified coke-oven gas in combination with tar will always give a waste gas below 0.0326 per cent. sulfur dioxide. With unpurified gas, the waste gas will always be above this figure. The following table shows the concentrations of sulfur dioxide in the waste

gases, using different proportions of tar and purified and unpurified coke-oven gas.

		Per Cent. of Sulfur Dioxide in Waste Gas	
Coke-oven Gas, Cu. Ft.	Tar, Gallons	Coke-oven Gas Purified	Coke-oven Gas Unpurified
13,000	0	0.00	0.134
11,500	5	0.0038	0.123
10,000	10	0.0077	0.111
8,500	15	0.0114	0.100
7,000	20	0.0154	0.088
5,500	25	0.0191	0.077
4,100	30	0.0225	0.065
2,600	35	0.0264	0.054
1,100	40	0.0300	0.043
0	44	0.0326	0.0326

From this table, the extent of desulfurization and resulfurization may be calculated by the same method used previously. Take, for example, a combination of 7000 cu. ft. of completely purified coke-oven gas and 20 gal. of tar. The sulfur in the slag in equilibrium with the waste gas from this combination is, from Fig. 1, 0.055 per cent. sulfur. The average driving force for the expulsion of sulfur from the slag will be 0.100 − 0.055 = 0.045 per cent. sulfur. The total amount removed will be, from the equation $S = K \times A \times (S - S_e) \times \theta$,

$$0.0040 \times 450 \times 0.045 \times 480 = 39 \text{ lb. sulfur.}$$

The total amount of sulfur allowable in the charge will be, as before, sulfur at end + sulfur removed, 72 + 39 = 111.0 lb. The scrap contains 46 lb., therefore, the hot metal can contain 65 lb., which gives a hot metal with 0.056 per cent. sulfur.

In this system of clean coke-oven gas and tar, the net saving for any combination may be calculated by the method used on coke-oven gas alone. In using unpurified coke-oven gas and tar, the amount of sulfur picked up by the slag can be calculated in a similar manner, except that in this case the sulfur concentration will be constantly building up in the slag instead of being kept low. It may be noted here that a combination of 25 gal. of tar and 5500 cu. ft. of unpurified coke-oven gas correspond, with respect to sulfur in the waste gas, to producer gas from a coal containing about 1.2 per cent sulfur.

Use of Partly Cleaned Coke-oven Gas Alone

If it were desired to eliminate only time lost through high-sulfur heats, the gas need not be purified to more than 125 to 135 gr. per 100 cu. ft. This would cost slightly under 0.50 cents per 1000 cu. ft., but

for the purpose of illustrating the saving in this case the cost will be taken at that figure.

Time Lost per Furnace per Month, Hours	Dollars per Ton Saved Eliminating Lost Time	Cost of Cleaning, Dollars per Ton	Net Saving, Dollars per Ton
0	0.000	0.065	−0.065
1	0.010	0.065	−0.055
2	0.019	0.065	−0.046
5	0.049	0.065	−0.016
10	0.098	0.065	+0.033
15	0.146	0.065	+0.081
20	0.195	0.065	+0.130

If unpurified coke-oven gas with 500 gr. of sulfur is used, the time lost through high-sulfur heats will be very large, the total time being a function of the sulfur in the charge.

Conclusions

1. A direct ratio exists between the concentration of sulfur dioxide over the bath and the amount of sulfur picked up by the scrap during melting.

2. A direct ratio also exists between the concentration of sulfur dioxide over the bath and the concentration of sulfur in a slag containing lime, when sufficient time has been allowed for equilibrium to be established.

3. The ratio between the gas and the oxide formed on melting is

$$\frac{\text{vol. per cent. } SO_2 \text{ in gas}}{\text{per cent. S in oxide}} = \text{about } 0.90$$

The ratio between the gas and slags containing lime is

$$\frac{\text{vol. per cent. } SO_2 \text{ in gas}}{\text{per cent. S in slag}} = 0.270$$

4. The rates of sulfur absorption and of desulfurization are equal and have a numerical value of about 0.004 lb. of sulfur absorbed or lost per minute per square foot of slag-gas surface per unit of concentration difference (per cent.) between the sulfur in the slag and the sulfur that would be in equilibrium with the gas over the slag.

5. The use of a gas free from sulfur will allow a much higher percentage of sulfur in the charge of an open-hearth furnace.

6. The use of a gas free from sulfur will prevent the loss of time due to high-sulfur heats encountered in present operation.

7. Sulfur-free gas will be economical under certain conditions as it will allow a higher sulfur and, therefore, cheaper pig iron to be used and as there will be no time lost on high-sulfur heats.

8. The economy in using sulfur-free coke-oven gas is much greater than in using sulfur-free producer gas, on account of the larger volumes of producer gas which must be purified.

9. There is a direct loss in using sulfur-free producer gas unless the time lost on high-sulfur heats is above 1.5 per cent. of the total working

time. Clean coke-oven gas is economical under almost all conditions. The exceptions are when low-sulfur charges are in use and when the time lost on high-sulfur heats is very small, using these low-sulfur charges.

10. When burning any fuel in the open hearth, the waste gases should not exceed 0.035 per cent. sulfur dioxide if sulfur absorption is to be avoided. When coke-oven gas and tar are burned together, the coke-oven gas should be cleaned to 125 to 135 gr. of sulfur per 100 cu. ft. of gas if high-sulfur heats are to be avoided. If very large amounts of tar are used, 30 gal. per ton of steel, with the coke-oven gas, the sulfur content of the latter may be raised to approximately 150 grains.

Acknowledgment

The author wishes to acknowledge the kindness of Mr. F. W. Sperr, Jr., of the Koppers Co., in supplying data on gas cleaning; of the Western Electric Co., in supplying the electrolytic iron for the experiments in the small furnace; and to express his appreciation of the assistance of Messrs. E. Harris and K. Flint, of the Massachusetts Institute of Technology School of Chemical Engineering Practice in obtaining the data on heat 26-P-380.

DISCUSSION

Henry D. Hibbard,* Plainfield, N. J.—Did not most of the sulfur in the gas get in from sulfur that is in the form of H_2S?

C. H. Herty, Jr.—The sulfur in the fuel gas is H_2S, but H_2S, like CO or hydrogen, is oxidized in the furnace. In lime solutions, for instance, SO_2 is picked up just as readily as H_2S forming calcium sulfite. In this case we probably form calcium sulfide.

L. F. Reinartz,† Middletown, Ohio.—What relationship was found to exist between the iron oxide content of the slags and their power to absorb sulfur? I have found that the higher the iron oxide concentration in the slag the lower is its power to absorb sulfur. In fact, in concentration of about 40 per cent. iron oxide and extremely low-carbon material, it is difficult to cause any more sulfur to go in the slag despite the fact that you have sulfur-free gas, for instance natural gas. A point is reached where, unless you are able to increase the lime content of that bath, the sulfur concentration of the slag cannot be decreased.

It has been said that the gas checkers would be considerably less clogged if we had clean gas. I cannot check that up with our experience because we have many times analyzed deposits in gas checkers but at no time have we found any carbon deposit; it is always a red oxide of iron.

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* Consulting Engineer.

† Assistant General Superintendent, American Rolling Mill Co.

In the case of producer gas, this iron oxide, especially in the gas checkers, runs extremely high in sulfur, showing that the sulfur has been absorbed.

C. H. Herty, Jr.—The FeO in the slag prevents the absorption of sulfur from the metal. If there is any equilibrium or ratio between the slag and the metal, the higher you make either of these iron oxides the more you drive back the reaction. When you get to 40 or 45 per cent. FeO, you are tending to drive the reaction back that way. We found that very thing where we had a slag that ran about 30 or 40 per cent. The analysis given is on the electric furnace run, 28 per cent. FeO and 4 per cent. Fe_2O_3 at the same time. With high FeO in the slag, you cannot desulfurize the metal, because you tend to reverse your desulfurization reaction. We have investigated the gas checker and found that the bricks in the gas checker are always coated with a thick film of solid, apparently solid, carbon embedded in the brick.

L. F. Reinartz.—We have a deposit of black iron oxide and have never found more than 0.2 per cent. carbon in this deposit.

C. H. Herty, Jr.—Do you not find a sort of glassy covering?

L. F. Reinartz.—There is a covering of iron oxide on the outside about ½ or ¾ in. thick. I have never been able to find the slightest particle of carbon.

C. H. Herty, Jr.—That is remarkable, because in our air checkers we find this glassy covering which is absolutely the same color as the brick; it may be a little darker. In the gas checkers, the same glassy covering, which is a little thicker, is pitch black and very resistant to heat. From a qualitative study of furnace performance the black deposits seem to have a wonderful power for resisting heat flow.

Ancel St. John,* New York, N. Y.—If that material on the surface of the brick is a pitch or carbon material, by putting it through an experimental process similar to that used in the manufacture of artificial graphite it should be possible to develop a graphitic structure that can be identified very readily by various methods; probably the simplest is by x-ray analysis. To determine facts about the nature of materials, etc. in brick or elsewhere without destroying or affecting the material in any way, x-ray analysis is rather valuable. The sample is put into the crystallometer and subsequently is taken out; if the chemical analysis of that particular piece is desired it can be obtained. I have repeated examinations on samples at intervals over a period of months or even years and have followed spontaneous changes that are taking place in the exact piece that I had examined previously.

* Consulting Physicist.

A. L. FEILD,* New York, N. Y.—The authors have brought to bear on this subject of sulfur elimination and absorption an entirely new viewpoint and have conclusively shown that the two phenomena are manifestations of the same physico-chemical equilibrium. Open-hearth men have realized for years that they could eliminate sulfur in the basic furnace, but textbooks do not indicate how this elimination proceeds except for the customary statement that lime combines with sulfur to form calcium sulfide. There is no statement explaining why, under certain conditions, sulfur elimination does not occur.

It has also been known that sulfur is picked up from the furnace gases, but open-hearth men in attempting to eliminate sulfur have followed cut-and-try methods. They have held their heat and they have run with a high-lime slag without paying very much attention to the composition of the furnace gas. Undoubtedly in many cases heats have been prolonged under conditions where the composition of the gas precluded any appreciable sulfur elimination. By means of the curve contained in this paper, it is possible for an operator to determine at once whether he will be able to eliminate appreciable sulfur and just how much elimination can be realized in the end. I know of no open-hearth reaction that has been studied with the care and success that characterizes the present investigation.

C. R. HAYWARD,† Cambridge, Mass.—Does it take very much time to obtain this equilibrium?

C. H. HERTY, JR.—That depends entirely on the rate, but you can calculate the time from the absorption coefficient. It depends on the distance from equilibrium, agitation, physical conditions, and amount of slag present.

RALPH H. SWEETSER,‡ Columbus, Ohio.—If it is apparently so easy to take sulfur out of the open-hearth furnace, why can we not take the sulfur out in the blast furnace?

L. F. REINARTZ.—One speaker has said that it is difficult to get low sulfur in producer gas because low-sulfur coal is not as common as we would like to have it; therefore by trying to take sulfur out of the metal and putting it in the slag, we are opposing the reaction by which the sulfur from the gas is going into the slag. When we try to eliminate sulfur, the composition of the slag has a great bearing on this reaction. The analysis must be such that it will hold whatever sulfur we take out of the metal. The time taken to eliminate sulfur depends, to a great extent, on the quality of the slag we have. Slag that is high in lime, low

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in iron oxide, and fluid will take out the sulfur much more rapidly than a slag higher in iron oxide and lower in lime.

C. D. KING, New York, N. Y.—About 8 years ago, in the Pittsburgh district, some 65-ton natural-gas furnaces were operated, using approximately a charge of 6 per cent. limestone, 60 per cent. basic hot metal, and 40 per cent. scrap, with sufficient ore to suit. The iron ran approximately 1 per cent. manganese, 1.25 per cent. silicon, and 0.035 per cent. sulfur, and the steel as a rule finished around 0.035 per cent. sulfur. A few years later, because of the shortage of natural gas in that district, half of the shop was put on pulverized coal. The limestone charge was raised to approximately 10 to 12 per cent., the coal used being 600 to 700 lb. per ton of steel and analyzed close to 1 per cent. sulfur. With practically the same charge as the natural-gas furnaces, limestone excepted, the heats made on pulverized coal averaged about 13 points sulfur higher than the natural-gas furnaces.

Shortly afterwards, the pulverized coal was replaced by coke-oven gas, and natural gas also was replaced by the same fuel some time later. Using approximately the same charge of pig iron and scrap, but increasing the limestone charge to 8 or 9 per cent., as against the 6 per cent. on natural gas, coke-oven gas and tar furnaces finished as a rule 7 points sulfur higher than natural gas. The results obtained at this particular plant were verified by independent investigation at other plants using the same fuel. The tar analyzed about 0.50 per cent. sulfur per gallon and the gas about 0.75 lb. H_2S per 1000 cu. ft. The fuel ran approximately 6,500,000 B.t.u.'s per ton of steel, the gas being calculated on a 500 B.t.u. per cu. ft. basis and the tar 160,000 B.t.u. per gal. Although the practice was to use tar in melting down in times of stress, when the sulfur in the pig iron necessitated the most careful methods, and finishing up with coke-oven gas and tar, one furnace operated on coke-oven gas alone and showed remarkable finishes in sulfur in steel, as compared to the rest of the plant, which was operating on tar and gas. Although using somewhat less limestone and a slight decrease in the amount of pig iron charged, over long periods of time this furnace finished with as low or lower sulfur in steel as the combination coke-oven gas and tar furnaces, in spite of the fact that the influence of the sulfur in coke-oven gas is considered greater than that of tar for the same British thermal units.

On page 530, where a sulfur balance is worked out, it states that hot metal can contain 65 lb. of sulfur which, therefore, will permit the use of 0.056 per cent. sulfur in pig iron. Other instances are given where even higher sulfur in the pig iron is permissible. Although it is quite possible, from an experimental standpoint, to use such high sulfur in pig iron with relatively high pig iron charges, the added expense and extraordinary measures taken to prevent high-sulfur finishes in steel so far in basic

open-hearth operation have not proved fruitful and economical in actual practice. Even with the use of a fuel like natural gas, containing no sulfur, any excessive sulfur in the pig iron will be reflected in the finished steel, as the basic open-hearth furnace has not yet proved to be more than a very uncertain factor in desulfurization.

C. H. Herty, Jr.—Our experience along the lines mentioned by Mr. King, as far as gas is concerned, has given somewhat different results. When 10,000 cu. ft. of uncleaned coke-oven gas has been used per ton of steel, it has been found impossible to make steel to meet specifications; but as soon as that gas is cleaned down to 100 or 125 gr. sulfur is easily eliminated. It looks as though there are two cases where the facts are the same, but the results are different.

C. D. King.—That is, you are willing to spend some money in desulfurizing high-sulfur coke-oven gas so that you can manufacture a steel that the customer will accept. That may be a good prospect where it is not possible to secure anything other than high-sulfur pig iron, but it appears much more advisable to do desulfurization where reducing conditions exist, as in the blast furnace, rather than in the oxidizing condition of the open-hearth furnace.

Pig iron should take first place in its relative importance as regards sulfur in the finished steel, and any reduction in sulfur that can be effected in the blast furnace is most certainly advisable for good, normal open-hearth operation. This has proved true in natural-gas furnace practice, and even were the coke-oven gas reduced to nil in sulfur this would still hold true. Certainly its importance cannot be overlooked when the coke-oven gas contains some sulfur. However, even with natural gas containing no sulfur, experience shows that it is practically impossible to finish a 0.056 per cent. pig iron using 60 per cent. or more, pig iron under 0.40 per cent. sulfur, without resorting to exorbitant and expensive measures, which preclude their use for other than experimental purposes. When all has been said and done, it may be possible by the use of much labor, time, and money to produce a steel with sulfur acceptable to the customer, using high-sulfur pig iron, but such added expense might prove ruinous from a standpoint of plant operation. In other words, the expenditure of a little money at the blast furnace can affect a pig iron allowing a low-sulfur finish in steel, whereas much more would be spent at the open hearth to transform a high-sulfur pig iron into an acceptable low-sulfur steel.

C. H. Herty, Jr.—The only answer I have is that when this coke-oven gas was cleaned down to 50 gr. of sulfur, which is very low, they had no trouble in getting down to 12 points sulfur in their steel; the materials in the charge contained about 40 to 45 points sulfur.

C. D. King.—That was with a basic open-hearth furnace?

C. H. Herty, Jr.—Yes; with about 10 per cent. limestone. The total time for refining was 11 hr. I cannot understand how the two things can be comparable.

C. D. King.—Finishing 0.012 per cent. sulfur in a basic open-hearth furnace is well worth while talking about. Even with the ideal reducing conditions of an electric furnace this is considered very fine practice.

C. H. Herty, Jr.—We ran a test last fall on a sulfur balance throughout a heat; it melted about 85 points carbon and was pretty hot; we used two boxes of ore and got a very violent reaction. It looked like a spray chamber. We cut the gas off for 6 min. but let the air flow right through the furnace; during that time the furnace lost 11 lb. of sulfur to the air over the bath. We eliminated from 39 points down to 22 points of sulfur in 1½ hr. immediately following that period, the total sulfur in the furnace being constantly lowered in that time.

L. F. Reinartz, Middletown, Ohio.—We have had many years' experience with fuel oil, natural gas, and producer gas. Natural-gas heats will finish anywhere from 0.005 to 0.007 per cent. lower in sulfur than the producer-gas heats, when there is about 0.70 to 0.90 per cent. sulfur in the coal. When the coal runs up to 1.25 per cent. sulfur, the variation will be about 0.009 to 0.010 per cent. In the case of fuel oil, which contained about 0.15 per cent. sulfur, we had about 0.004 to 0.006 per cent. more sulfur in the steel than with the natural-gas heats. For many years, our practice has been to use about 10 per cent. limestone charge. When using natural gas, it was possible to get down to 0.023 to 0.024 per cent. sulfur on a charge containing not quite as much pig iron as the previous speaker used, I would say about 50 per cent. pig iron and 50 per cent. scrap. The sulfur in the pig iron probably ran about 0.035 per cent.; and in the scrap about 0.03 per cent. When using producer gas, the sulfur was about 0.007 per cent. higher in the finished product.

It is a rather remarkable statement to say that in an open-hearth furnace with the charge given by the author it is possible to get down to 0.012 per cent. sulfur. I have seen many analyses from many steel plants, but nothing that would approach such results. It is possible with natural gas to get down to 0.20 per cent. sulfur quite easily. It costs from $60 to $70 an hour to run an open-hearth furnace. If you add 3 or 4 per cent. limestone to the charge, it is apt to increase the time of the heat about 2 hr. For that reason, it is cheaper to take out the sulfur in the pig iron. Where it costs several dollars to remove sulfur in the open-hearth furnace, especially if you have an uncertain fuel, the blast furnace can do it for 50 cents to $1. All you must do in that case is to spend a little more money on coke and use a little bit more limestone. When that is interpreted back into steel, it amounts to about 25 cents per ton of steel.

HAAKON STYRI,* Philadelphia, Pa.—When two men state that the melting conditions are exactly alike, but the results are entirely different, I would say that the melting conditions are not alike. It would be advisable, if it were possible, to obtain records of the temperature in the furnaces, the composition of the slag and the steel, and the time for refining at the particular temperatures before the steel is finished. I am sure from other experimental data that one plant was worked at a higher temperature than the other, and it is well known that all reactions go much more quickly when the temperature is higher.

C. D. KING.—When coke-oven gas and tar were first used at this plant, it appeared that the additional sulfur in the steel, due to this type of fuel, was 7 points; it might be possible to show that there was a greater relationship between the fuel used on the sulfur in the steel than the influence of the pig-iron sulfur. Considerable data were collected on fifteen furnaces and for the first ten days the curve for sulfur in the finished steel followed the curve for the coke-oven gas with remarkable regularity. However, the pig iron for this period ran close to 0.040 per cent. of sulfur without any perceptible variations. At about this time, the blast furnaces reacted severely and started to cast some rather irregular iron, the sulfur varying from 0.030 to 0.070 per cent. It is unnecessary to state that this variation affected the sulfur in the steel very drastically, so much so that it was almost possible to superimpose the curve for sulfur in the steel on that for sulfur in the iron.

A year or so later, the blast furnaces, over long periods, ran around 0.030 per cent. sulfur in the pig iron and with a 60 or 65 per cent. pig iron charge in the open-hearth furnace, the steel consistently finished under 0.040 per cent. sulfur. In other words, the sulfur in the pig iron had a direct and immediate influence on the sulfur in the steel, whereas the sulfur in the fuel added its usual 7 points to the steel, but rarely, as far as could be proved, much more or less.

GEORGE A. ORROK, New York, N. Y.—I agree with the speaker regarding the use of coke-oven gas in the open hearth. In investigations covering ten or twelve furnaces, I was unable to find any relation between sulfur in the coke-oven gas and the sulfur in steel; that is, the sulfur in the steel followed more or less the sulfur in the charge, and apparently was not contaminated by sulfur in the coke-oven gas or by a change of fuel to either tar or fuel oil.

C. D. KING.—I did not intend to give that impression. I specifically stated that the pulverized coal added about 13 points sulfur to the steel and the coke-oven gas about 7, but with the coke-oven gas adding its 7 points the relative variations in the sulfur of the pig iron were more

* Chief of SKF Research Laboratory.

emphatic and clear cut than any variations caused by the amount of sulfur from the fuel, either in analysis or in the amounts of fuel used.

C. H. Herty, Jr. (author's reply to discussion).—A probable explanation of the small amount of desulfurization taking place when natural gas was used on the 65-ton furnaces mentioned by Mr. King, is in the weakly basic slag which these furnaces must have carried. A simple calculation of the amounts of lime and silica in the slags resulting from the charges given shows a ratio of lime to silica equal to 2. As is shown in the text, it is necessary to have a very basic slag to insure the slag taking the sulfur from the metal as fast as the gas removes the sulfur from the slag; in the heats with natural gas, this could hardly have been the case with the low ratio of CaO to SiO_2.

Reaction between Manganese and Iron Sulfide

C. H. Herty, Jr.* and O. S. True,† Lackawanna, N. Y.

(New York Meeting, February, 1925)

It is well known that manganese will desulfurize molten iron through the formation of manganese sulfide, which, being only slightly soluble in the metal, rises to and enters the slag where it remains as such (mixer slag) or is converted partly or wholly to calcium sulfide (basic open-hearth slag). The reaction by which manganese sulfide is formed is $Mn + FeS = MnS + Fe$. This reaction is generally considered to be reversible, although McCance[1] states that such is not the case. The experimental work was carried out to confirm the results of Röhl[2] as to the reversibility of the reaction.

Six trials are herein considered. In each 200 gm. of electrolytic iron free from manganese and sulfur were melted in a pure zirconia crucible in a carbon resistance electric furnace. To the melted iron in runs 2, 3 and 4 metallic manganese and manganese sulfide were added to give 1, 2 and 4 per cent. manganese respectively, with 0.50 per cent. of sulfur in each. In runs 5, 6 and 7, metallic manganese and iron sulfide to give the same proportions of manganese and sulphur as in runs 2, 3 and 4, were added. The melts were held molten in the furnace for an hour and then cast into small ingots.

The results of these melts are as follows:

Run	Material Charged	Ingredients of Manganese, Per Cent.	Charge Sulfur, Per Cent.	Analysis of Manganese, Per Cent.	Ingot Sulfur, Per Cent.
2	MnS + Mn	1.0	0.452	0.636	0.367
3	MnS + Mn	2.0	0.50	1.57	0.310
4	MnS + Mn	4.0	0.50	2.81	0.230
5	FeS + Mn	1.0	0.50	0.647	0.397
6	FeS + Mn	2.0	0.50	1.45	0.374
7	FeS + Mn	4.0	0.50	2.73	0.195

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† Massachusetts Institute of Technology, Master's Thesis, 1923.

1 Andrew McCance: Non-metallic Inclusions. *Jnl.* Iron and Steel Inst. (1918) **97,** 239.

2 G. Röhl: Constitution of Sulphide Enclosures in Iron and Steel. *Carnegie Sch. Mem.,* Iron and Steel Inst. (1912) **4,** 28.

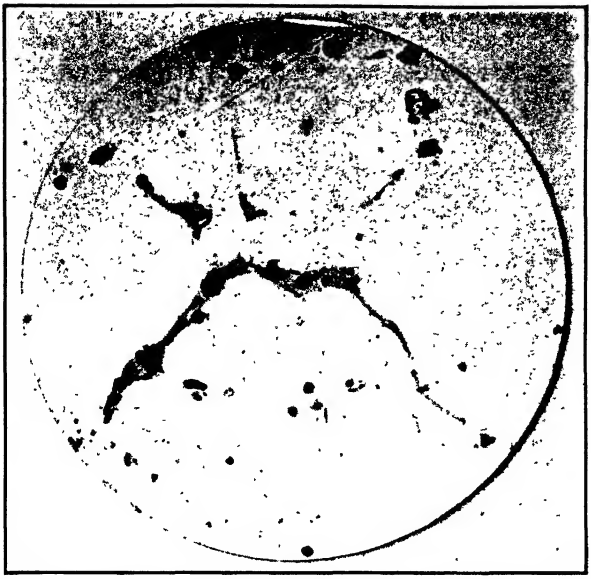

FIG. 1.—RUN 2, CONTAINING 0.636 PER CENT. MANGANESE AND 0.367 PER CENT. SULFUR. × 500.

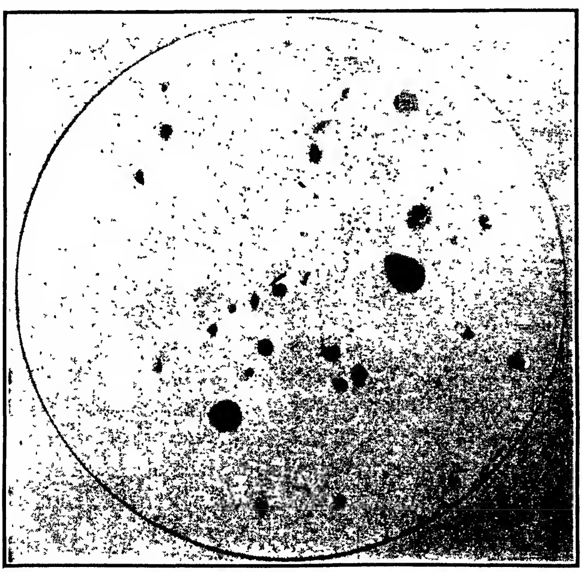

FIG. 2.—RUN 3, CONTAINING 1.57 PER CENT. MANGANESE AND 0.310 PER CENT. SULFUR. × 500.

These results show that manganese sulfide, even in the presence of an excess of manganese, will be converted to iron sulfide and enter the metal, the reaction, therefore, being reversible. Further, the greater the excess of manganese the lower the sulfur in the metal, regardless of whether the sulfur is originally present as MnS or as FeS. Comparing

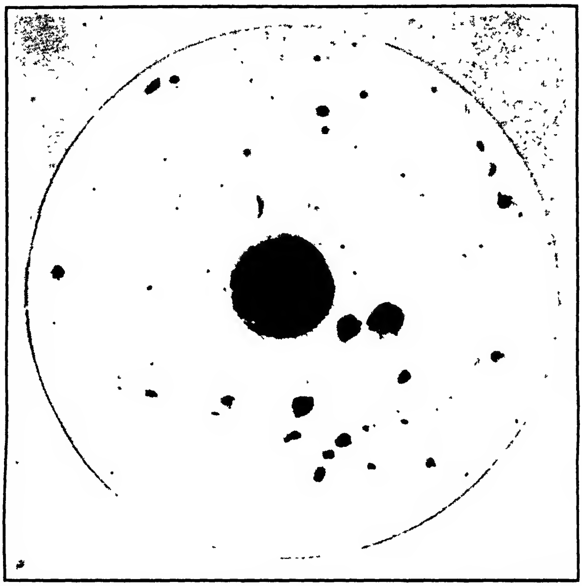

FIG. 3.—RUN 4, CONTAINING 2.81 PER CENT. MANGANESE AND 0.230 PER CENT. SULFUR. × 500.

the tests made with the same concentrations of manganese and sulfur in the charge, but with the sulfur charged as MnS in the first case and FeS in the second, we have:

Run	Material Charged	Charge: Manganese, Per Cent.	Charge: Sulfur, Per Cent.	Ingot: Manganese, Per Cent.	Ingot: Sulfur, Per Cent.
2	MnS + Mn	1.0	0.452	0.636	0.367
5	FeS + Mn	1.0	0.50	0.647	0.397
3	MnS + Mn	2.0	0.50	1.57	0.310
6	FeS + Mn	2.0	0.50	1.45	0.374
4	MnS + Mn	4.0	0.50	2.81	0.230
7	FeS + Mn	4.0	0.50	2.73	0.195

From these results, it is evident that equilibrium had been established, for regardless of the charging conditions, tests with equal concentrations of manganese and sulfur in the charge should come to the same final concentrations if the reaction $FeS + Mn = MnS + Fe$ is reversible.

Sections of the ingots from runs 2, 3 and 4 are shown in Figs. 1, 2, and 3. As the manganese excess increases the inclusions become darker,

showing that the ratio of manganese sulfide to iron sulfide increases. This is to be expected as the equilibrium constant or ratio for the reaction is

$$K = \frac{(\text{MnS})\text{ metal}}{(\text{FeS})\text{ metal} \times (\text{Mn})\text{ metal}}$$

from which it can be seen that as the concentration of manganese is raised the ratio $\frac{(\text{MnS})\text{ metal}}{(\text{FeS})\text{ metal}}$ must increase.

The authors wish to express their appreciation to Mr. V. O. Homerberg, of the Massachusetts Institute of Technology, for the preparation of the photomicrographs.

NOTE.—The loss of manganese over that required to form MnS was the result primarily of oxidation of manganese, the electrolytic iron containing 0.44 per cent. oxygen as surface oxidation picked up during pulverizing.

DISCUSSION

A. L. FEILD,* New York, N. Y.—The authors are to be commended on their attempt to establish qualitatively, by means of a method comprehensible to any student of elementary physical chemistry, the reversibility of the reaction $Mn + FeS \rightleftarrows MnS + Fe$ in molten steel as solvent. Obtainment of a criterion of reversibility from inspection of the ingot analyses was made possible because of the fact that a relatively high percentage of sulfide (equivalent to 0.45–0.50 per cent. sulfur) was added to the melts; sufficient in each case not only to cause the latter to become saturated with sulfide but to give rise to the formation or presence of an insoluble excess of manganese sulfide, which escaped from the metal bath. Briefly, the authors find that a decrease in total sulfur occurs with increase in the total manganese contents of the steel, regardless of whether the equilibrium represented by the above equation is approached from the right or from the left. It is also observed that, for equal percentages of manganese and sulfur in the initial charge, the final percentages of these elements in the ingot do not appear to have been influenced in any great measure nor in any systematic manner by the direction from which equilibrium is approached.

The authors state that this work was carried out to confirm the results of Rohl. Inasmuch as reversibility was observed, it is to be inferred that they consider the data of the paper under discussion a corroboration of the validity of Rohl's conclusions in contradistinction to the findings of McCance, who has held the reaction to be substantially irreversible. As a matter of fact, prior to the work of the authors, experimental data of the direct sort yielded no reliable criterion in favor of the existence of any substantial or practically important degree of reversibility. In so

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far as indirect data were concerned, by far the greater weight of evidence inclined toward two conclusions: (1) That the reaction proceeded toward the right to practical completion in the ideal case of the three-component system Fe-Mn-S with iron in large excess; and (2) that the presence of oxygen as a fourth component was responsible for that apparent reversibility which occurs to so marked a degree in ordinary steel practice. Recently I had other occasion to refer to this general subject,[3] so that repetition is unnecessary. The present paper brings forward the first reliable evidence of a direct sort to support the view that the reaction in question is reversible; credit for this accomplishment belongs to the authors.

Taking for granted the reversibility of the reaction, the next important step is to determine the equilibrium constant. If this constant is determined, we have a quantitative measure of the extent to which the reaction is reversible and a simple method for computing the final distribution of sulfur in its combination with iron, on the one hand, and manganese, on the other, for any given composition of iron or steel. Also, if the true solubility of manganese sulfide as such in liquid steel is known, final equilibrium within the molten metal for any given initial charge composition may be deduced.

Fortunately, it is possible to calculate the equilibrium constant, and also the solubility of manganese sulfide, on the basis of the analytical data obtained by the authors. The method of calculation employed is simple but would appear to be new, in metallurgical calculations at least. Consider the reversible reaction

$$\mathrm{FeS} + \mathrm{Mn} = \mathrm{MnS} + \mathrm{Fe} \tag{1}$$

to obtain in molten steel as solvent. As was actually the case in the present investigation, assume that the liquid is saturated with manganese sulfide. Take any two experimental runs, say runs 2 and 4:
Let,

u_1 = molal percentages of iron sulfide at equilibrium in run 2;
m = molal percentages of dissolved manganese sulfide at equilibrium in run 2;
x_1 = molal percentages of "free" or uncombined manganese at equilibrium in run 2.

Let u_2, m, and x_2 represent the corresponding values in the case of run 4. Now the molal percentages of total manganese are equal to 0.645 and 2.85 and total sulfur to 0.637 and 0.400 for runs 2 and 4, respectively; then,

$$x_1 + m = 0.645 \tag{2}$$

and

$$m + u_1 = 0.637 \tag{3}$$

[3] *Trans.* (1923) **70**, 221–23.

Similarly,

$$x_2 + m = 2.85 \tag{4}$$

and

$$m + u_2 = 0.400 \tag{5}$$

Also, from the law of mass action

$$x_1u_1 = x_2u_2 = C \tag{6}$$

where C is a constant.

Solving the five equations for the five unknown quantities involved,

$$u_1 = 0.267, x_1 = 0.275, u_2 = 0.0295, x_2 = 2.48, \text{and } m = 0.370.$$

These values are expressed in terms of molal percentages for the liquid phase at equilibrium, which equilibrium is supposed to be fixed, or "frozen," by the rapid chilling of the small ingots and thus preserved in the solidified melt.

The data on runs 2 and 4 lead directly to the conclusion that the molal ratio of manganese sulfide to iron sulfide at equilibrium is equal to 1.4 and to 12, respectively, for runs 2 and 4, and that the actual molal percentages of iron sulfide are equal to 0.27 and to 0.03, respectively. The molal percentage of manganese sulfide is, in both cases, equal to 0.37, which also represents the solubility of manganese sulfide in the melt. The value for C, the constant of equation (6), is equal to 0.0732. This constant is closely analogous to the "solubility product" of Nerst, which has been so useful in interpreting the behavior of ionized salts in aqueous solutions.

It is now possible to calculate the value of the equilibrium constant K for the reaction of equation (1). For practical purposes the molal percentage of iron is constant and may be placed at 98.0 (actually it is equal to 99.00 for run 2 and to 96.95 for run 4). Then,

$$K = \frac{98.0\, m}{ux} = 496 \tag{7}$$

Values for the constant m, C, and K have been similarly calculated from the data of several other pairs of runs. The results are shown in the table below:

Source of Data	m	C	K
Runs 2 and 3	0.527	0.0130	3970
Runs 2 and 4	0.370	0.0732	496
Runs 5 and 7	0.272	0.1665	160
Runs 3 and 4	0.250	0.3895	63

Of course, if the experiments of the authors had been carried out under ideal conditions, the values for m, C, and K should be constant throughout the series and independent of the particular set of data selected.

It is not possible to state whether or not the inconstancy of m, C, and K is due chiefly to the combined effect of variability of temperature,

analytical and sampling error, and failure to attain equilibrium. It is to be hoped that the work of the authors will be repeated in an effort to obtain greater refinement of method and to avoid, as far as practicable, the above-mentioned sources of possible error. The above-described method of calculating the equilibrium constant now supplies a criterion for evaluating experimental accuracy and reliability of technique.

Examination of the calculated values in the preceding table leads to the conclusion that the author's data, while valuable from the qualitative side, are not sufficiently exact to permit of a reliable quantitative estimate of the value of the equilibrium constant. There would appear to be a decided tendency for K to decrease in magnitude with increasing percentages of manganese. This consistent drift toward lower values of equilibrium constant may be due either to an effect of uncombined manganese in decreasing the solubility of manganese sulfide, or to the presence of emulsified manganese sulfide under equilibrium conditions. The latter appears to be the more probable.

Let us suppose that another reversible reaction of analogous character and represented by the equation

$$Mn + FeO \rightleftarrows MnO + Fe \tag{8}$$

obtains in the melt. With the percentages of manganese actually present in these runs, it is certain that the steel would be saturated with MnO at equilibrium.

Let, u' = molal percentage of dissolved FeO;
x = molal percentage of uncombined Mn;
m' = molal percentage of dissolved MnO;

then

$$K' = \frac{98.2\, m'}{u'x} \tag{9}$$

and

$$C' = u'x \tag{10}$$

Where K' is the equilibrium constant for equation (8) and C' its "solubility product." From (7) and (9),

$$\frac{u}{u'} = \frac{mK'}{m'K} = \text{constant} \tag{11}$$

In other words, the molal percentage of dissolved iron sulfide, FeS, must bear a constant ratio to the molal percentage of dissolved iron oxide, FeO, under the conditions of these experiments; *i.e.* when the melt is saturated with respect to both MnS and MnO. This fact indicates, incidentally, how difficult it is to consider the sulfur-binding power of manganese apart from its concomitant effect on any oxygen that may be present. Obtainment of values for the equilibrium constant for equation (8) and the solubility of manganese oxide is theoretically possible by means of a calculation of the same type as that already applied to equa-

tion (1). The only additional datum required is the total molal percentage of oxygen dissolved at equilibrium in the melt in the form of the oxides of iron and manganese. By an obvious alteration of the method of calculation, a knowledge of the molal percentage of oxygen existing in solution as iron oxide would serve as well.

H. S. Rawdon,* (Washington, D. C.).—The photomicrographs show somewhat more than the author has pointed out and help to confirm his conclusions based on other evidence. Fig. 1 represents a heat in which manganese was relatively low. The manganese content is increased in runs 2 and 3 so that Fig. 3 represents more nearly pure manganese sulfide than Fig. 1. We can state, with considerable assurance, that in Fig. 1 we have ferrosulfide, from the form of distribution in those inclusions. It is well known that iron sulfide exists in steel as thin intercrystalline films. As the manganese content was increased, therefore, iron sulfide changed over into manganese sulfide, and the thin films were changed into the well-formed globules in Fig. 3, which condition is quite generally considered characteristic of manganese sulfide. I do not quite undersand why one should get a duplex structure in Fig. 3. It is clearly shown that there are two constituents especially in the large globule. That may indicate that instead of the iron and manganese sulfide forming a true solid solution they separate out as more or less distinct phases.

C. H. Herty, Jr.—I think very probably that is true although there is a small amount of iron sulfide in Fig. 3. Possibly two phases separate out. We were not able to check that.

T. L. Joseph,† (Minneapolis, Minn.).—The desirable thing in this case is to drive the reaction toward the formation of manganese sulfide. It is important to remove that manganese sulfide as quickly as possible. The solubility of manganese sulfide will affect this but I think the composition of the slag over the bath is very important. By providing the proper slag the manganese sulfide can be removed from the reaction. This will further desulfurization.

C. H. Herty, Jr.—Where we had a very small amount of manganese sulfide, if the sulfide were increased we would have gotten much less desulfurization for a given amount of manganese.

Haakon Styri,‡ Philadelphia, Pa.—Calling attention to the equilibrium reaction between manganese, oxygen and iron, it seems logical to assume similar relations if in such reaction sulfur replaces oxygen, except that sulfur and manganese may react with only one atom each. The relation between oxygen and manganese in molten iron can be represented

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* Physicist, Bureau of Standards.

† Metallurgist, Bureau of Mines.

‡ Chief of SKF Research Laboratory.

graphically on semi-logarithmic scale by two straight lines, the abscissa giving the concentrations; the ordinate, the log of the dissociation pressure as shown, where lines intersect the abscissa give corresponding equilibrium concentrations of oxygen and manganese.

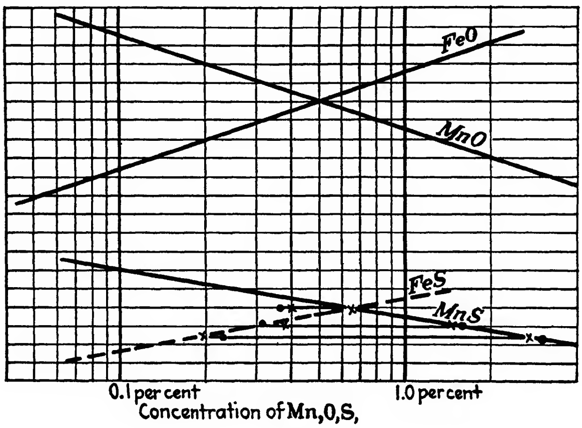

FIG. 4.

We can draw lines for sulfur and manganese and we must have a similar relation; the ordinates start at some arbitrary point. Taking the manganese concentration as a base and plotting the corresponding sulfur concentrations from the data in the paper, it will be found that they do not fall on a straight line. This may be due to having different temperatures for the various experiments, or insufficient time in some, or even different composition of the slag.

Reduction of Iron Ores by Carbon Monoxide

BY HEIHACHI KAMURA,* M. S., TOBATA-SHI, FUKUOKA-KEN, JAPAN

(New York Meeting, February, 1925)

THE reduction of iron oxide, such as Fe_2O_3, to iron in the blast furnace is performed principally by carbon monoxide, but partly by solid carbon by the two following reactions:

$$Fe_2O_3 + 3CO = 2Fe + 3CO_2$$
$$2Fe_2O_3 + 3C = 4Fe + 3CO_2$$

It is known that reduction by carbon monoxide takes place at a much lower temperature than reduction by carbon and that the reducing action of carbon monoxide progresses to the inside of the ore in lump form by gaseous diffusion. In the reduction by carbon, however, the reducing action takes place only at the contact surface of the ore and carbon, so that the more complete the reduction by carbon monoxide, the more efficient is the operation.

However, the reduction does not progress as shown in the foregoing equation, because carbon dioxide acts oxidizingly on the metallic iron to such a degree that when the gaseous composition reaches a certain proportion of carbon dioxide to carbon monoxide, the reduction practically stops, even though the gases are moving slowly through the heated ore. The proportions of carbon monoxide and carbon dioxide in the gas depend on the kind of iron oxide and the temperature of reduction, also on the duration of time in the reaction. The longer the time of the reaction, the higher the proportion of carbon dioxide obtained in the gas, but finally it will attain to a condition of equilibrium.

CHEMICAL EQUILIBRIUM OF IRON, OXYGEN, AND CARBON

Investigations concerning the equilibrium between iron, oxygen, and carbon have been carried out by E. Baur and A. Glaessner,[1] who deter-

* Metallurgist, Meiji Mining Co.
[1] *Ztschr. Phys. Chem.* (1903) 43.

mined the equilibrium conditions of the two reactions within the temperature range of 350° to 900°C.

$$Fe_3O_4 + CO \qquad 3FeO + CO_2 \tag{1}$$
$$FeO + CO \qquad Fe + CO_2 \tag{2}$$

Next investigations were made by Schenk and Heller,[2] and by Schenk, Semiller and Falcke[3] within the range of 550° to 700° C. Recently Professor Matsubara[4] has thrown light on the equilibrium at higher temperatures.

The total equilibrium between iron, iron oxide, carbon, and the two gaseous oxides, carbon monoxide and carbon dioxide, is represented as an equilibrium of a three-component system (C, Fe, O) with the simultaneous presence of a four-phase (Fe, FeO, C) gas. According to the phase rule, such a system must have one degree of freedom; the equilibrium is univariant. Therefore at a definite temperature, the pressure and the concentration of gas will be fixed. However, when there exist only three phases of iron, carbon and the gaseous phase, the equilibrium will be bivariant. If the temperature is fixed, the pressure and the concentration of gas will vary and it cannot be brought to the equilibrium condition until one of the phases is fixed. The equilibrium condition in the chemical equations (1) and (2) is called, respectively, Fe_3O_4–FeO and FeO–Fe equilibrium. When the reduction progresses the following Fe–Fe_3C and FeO–Fe_3C equilibriums will exist:

$$3Fe + 2CO \qquad Fe_3C + CO_2 \tag{3}$$
$$3FeO + 5CO \qquad Fe_3C + 4CO_2 \tag{4}$$

The composition of the gaseous phase in the four equilibriums given, which has been obtained by the investigators named, is as follows:

Temperature, Degrees C.	Fe_3O_4–FeO Equilibrium		FeO–Fe Equilibrium	
	Per Cent., CO_2	Per Cent., CO	Per Cent., CO	Per Cent., CO_2
561			53.6	46.4
627	43.5	56.5	57.0	43.0
662	39.7	60.3	58.4	41.6
720	35.2	64.8	60.7	39.3
863	25.5	74.5	65.9	34.1
963	20.4	79.6	69.2	30.8
1070	16.4	83.6	72.4	27.6
1175	15.2	84.8	75.5	24.5

[2] *Ber.* (1905) [3] *Ber.* (1907) **40.** [4] *Trans.* (1922) **67,** 3.

The percentages of CO in FeO–Fe_3C and Fe–Fe_3C equilibrium are as follows:

Temperature, Degrees C.	FeO–Fe_3C Equilibrium, Per Cent. CO	Fe–Fe_3C Equilibrium, Per Cent. CO
800	86.0	92.3
850	88.6	94.5
900	90.3	95.4
1000	92.9	97.0
1100	95.6	98.9

In Fig. 1, the curves indicate the composition of the gaseous phase against the temperature in the equilibrium conditions. The total

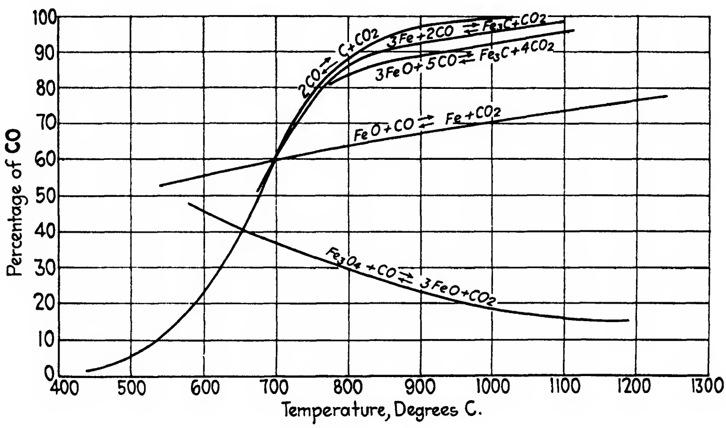

FIG. 1.

equilibrium condition in definite temperature between Fe, FeO, CO, and CO_2 is represented by the curve *A* in Fig. 2. On the left-hand side of the line, the metallic iron is oxidized to FeO, and on the right-hand side the reduction of FeO takes place. Curve *B* is the equilibrium in definite temperature between FeO, Fe_2O_3, CO, and CO_2; also *C* is the equilibrium between amorphous carbon, CO, and CO_2. At the intersection of the curves are the two equilibria between Fe, FeO, C, and two gaseous oxides. Each field between the lines has the following meaning:

Field I,	$2CO \rightarrow C + CO_2$	$FeO + CO \rightarrow Fe + CO_2$
Field II,	$2CO \rightarrow C + CO_2$	$Fe + CO_2 \rightarrow FeO + CO$
Field II′,	$2CO \rightarrow C + CO_2$	$FeO + CO_2 \rightarrow Fe_3O_4 + CO$
Field III,	$C + CO_2 \rightarrow 2CO$	$Fe + CO_2 \rightarrow FeO + CO$
Field III′,	$C + CO_2 \rightarrow 2CO$	$FeO + CO_2 \rightarrow Fe_3O_4 + CO$
Field IV,	$C + CO_2 \rightarrow 2CO$	$FeO + CO \rightarrow Fe + CO_2$

When Fe, FeO, C, CO, and CO_2 coexist, the reduction of FeO to Fe takes place in the fields I and IV. In field I, metallic Fe and C can

coexist; and in field IV, CO gas will be generated by the reduction of fine carbon. In fields II and II′, C and FeO or C and FeO with CO can coexist, respectively. However, in fields III and III′, C disappears by oxidizing action and FeO or Fe_3O_4 respectively is stable.

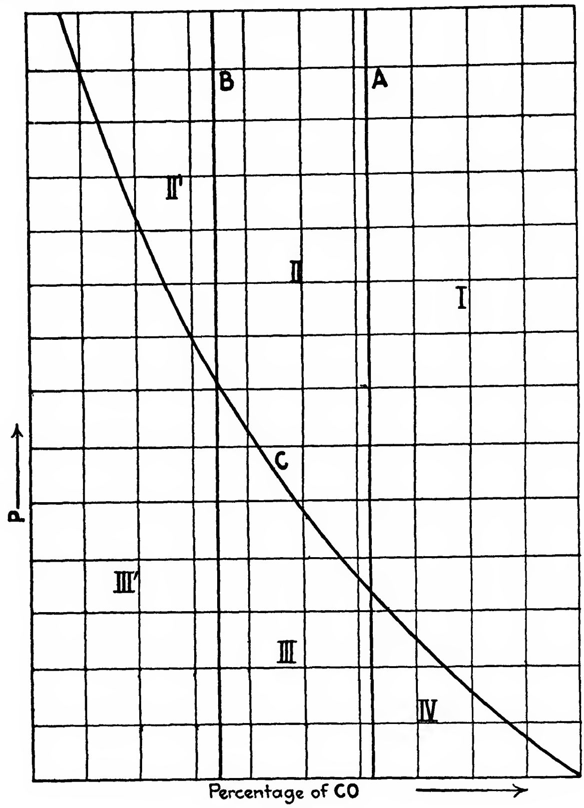

FIG. 2.

PROPER TEMPERATURE FOR REDUCTION

It has been understood that the oxide of iron can be reduced to the metallic state by carbon monoxide at a moderately lower temperature than in the blast furnace, considering the result of investigation of equilibrium. But from the technical standpoint, it is important to determine the temperature at which nearly perfect reduction takes place in moderate velocity. For this purpose, the author investigated the proper temperature of reduction on Mesabi hematite ore having following composition: 64.48 per cent. Fe, 4.56 per cent. SiO_2, 0.68 per cent. Al_2O_3, 0.059 per cent. P_2O_5.

The ore passed through screens 30 to 50 meshes per linear inch. The carbon monoxide gas was prepared by passing the carbon dioxide on the

charcoal which was heated to about 1000° C. The small percentage of carbon dioxide in the gas was absorbed by KOH solution and the moisture in it was taken off by passing through concentrated sulfuric acid; then nearly pure carbon monoxide gas was obtained.

The experiment of reduction was carried on in a combustion tube heated in a horizontal type of electric-resistance furnace of nichrome wire, as in Fig. 3. The temperature in the furnace was measured by a Pt-Rh thermocouple. From 0.5 to 1.0 gm. of the ore was put into an alundum boat, which was placed in the middle of the furnace. Rubber stoppers, into which glass tubes with cocks were inserted, stopped both

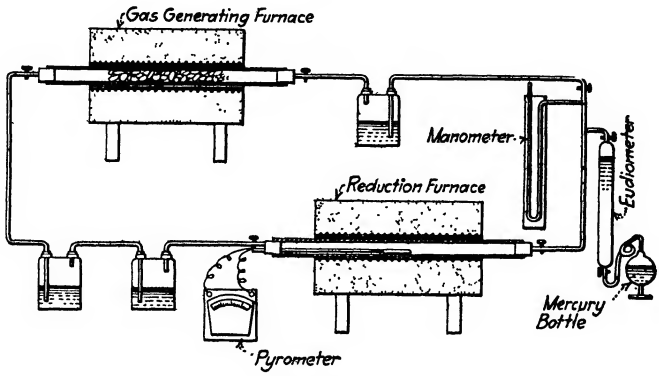

FIG. 3.

ends of the combustion tube. The air in the tube was evacuated as far as possible before starting the experiment. When a desired temperature was obtained, the CO gas was passed into the tube for reduction. The gas, taken in a eudiometer after reduction, was analyzed and the weight of reduced sample also was measured. In experiments 1 and 2, the reduction was carried on at 550° C. on 1 gm. of the hematite ore. After passing 1000 c.c. of CO, there was from 30 to 40 per cent. of CO_2 in the gas after reduction and a great deal of carbon was deposited on the surface of the ore. This was due to the dissociation of CO by the following reaction, according to the catalytic action of iron oxide:

$$2CO \rightarrow C + CO_2$$

In experiment 4, the reduction was done at 600° C. and 600 c.c. of CO gas was passed. The gas after reduction was analyzed in each 100-c.c. interval. The percentage of CO_2 in the first 100 c.c. of the gas was 38.2 per cent., and in the last interval, 29.0 per cent. Some of the deposition of carbon was recognized and the diminution of weight of the sample was only 0.0336 gm. As reduction of iron oxide to the metallic

state requires a higher temperature than the above, the following experiments at higher temperatures were made.

Number of Experiment	Weight of Sample, Grams	Temperature of Reduction, Degrees C.	Volume of CO Used, Cubic Centimeters	Per Cent. of Reduction		Per Cent. of CO_2	
				From Weight of Reduced Sample	By CO_2 in Reduction Gas	At Start	At End
8	1.0	700	1012	64.2	63.0	44.4	16.4
11	0.5	750	1242	87.6	85.0	40.0	14.4
14	0.5	800	1020	85.9	87.0	37.4	7.6
16	0.5	850	1300	93.5	94.0	37.0	4.0
17	0.5	900	1300	98.3	98.0	32.2	4.6
18	0.5	600	649	50.7	49.0	30.0	9.2

The time of reduction in these experiments was from 1 to 2 hr. The percentage of reduction was calculated from the diminished weight of the sample and also from the weight of O_2 combined with CO forming CO_2; the two results nearly coincide.

The results of the experiments show that the percentage of reduction at 600° C. was only 50 per cent. passing 600 c.c. of CO, and that if the reduction was carried farther, the carbon would deposit on the sample without any more reduction, as in experiment 4.

If the reduction temperature was higher than 600° C., the percentage of reduction was increased gradually by raising the temperature. For instance, at 700° C. it was 64.2 per cent., and at 800° C., 85.9 per cent., for about the same volume of CO. It increased to 93.5 per cent. at 850° C. and to 98.3 per cent. at 900° C. with the same volume of CO. At 900° C., nearly perfect reduction was obtained by 1300 c.c. of CO at standard conditions. Therefore we would say that the reduction of hematite to metallic state will take place at 900° C. at moderate velocity.

Rate of Reduction on Different Sizes of Ore

As the next step, experiments were made at a temperature of 900° C. on two sizes of Chushu hematite to detect any influence on the velocity of reduction by the size of ore; the ore analyzed as follows:

Size of Ore, Meshes per Linear Inch	SiO_2, Per Cent.	Fe as Fe_3O_4, Per Cent.	Fe as Fe_2O_3, Per Cent.	Total Fe, Per Cent.	CaO, Per Cent.	S, Per Cent.	P, Per Cent.	Mn, Per Cent.	Al_2O_3, Per Cent.
10–20	10.9	11.886	48.524	60.410	0.30	0.027	0.005	0.338	0.76
20–30	9.68	12.696	48.834	61.530	0.38	0.033	0.005	0.297	0.88

Some of the results were as follows:

Number of Experiment	Size of Ore, Meshes per Linear Inch	Time of Reduction		Volume of CO for Reduction, Cubic Centimeters	Per Cent. of Reduction	
		Hours	Minutes		By Weight	By O_2 Formed CO_2
5	20–30	2	30	1503	97.5	93.2
7	10–20	2	30	1198	95.2	92.9

After reduction the gas was analyzed at intervals and the curve shown in Fig. 4 plotted for the volume of CO used and the percentage of reduction calculated from the O_2 taken off by CO as CO_2. There is no evidence in these curves that the size of ore has any influence on the velocity of reduction. The ore in experiment 7 was larger than that in experiment 5, but the reduction progressed at nearly the same ratio against the volume of CO passed in the two cases.

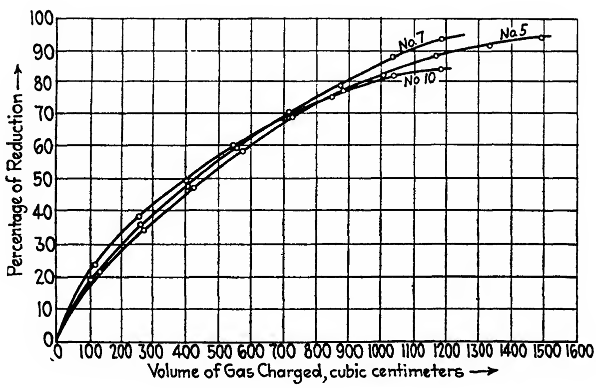

FIG. 4.

From these experiments it was decided that larger ore could be used, so the reduction of Santo hematite was tried. This ore passed through 10 to 4 meshes per linear inch and had the following composition: Fe 67.165 per cent., SiO_2 3.08 per cent., Al_2O_3 0.96 per cent., CaO 0.432 per cent., Mn 0.153 per cent., MgO 0.145 per cent., P 0.038 per cent., S trace, H_2O 0.10 per cent., ignition loss 0.84 per cent.

In these experiments, the weight of ore was much larger than in the previous experiments, and it required a much larger volume of gas, so that the author devised a system of gas circulation: The gases, which after reduction have some CO_2, are circulated again into the red-hot charcoal to reduce the CO_2 to CO. The circulation of the gases is maintained continuously to the reduction furnace until the experiment is finished.

A diagrammatic sketch of the arrangement is shown in Fig. 5. It differs from the arrangement shown in Fig. 3 by placing a blower between the gas-generating furnace and the reduction furnace and an aspirator at an end of system to take the volume of increased gas, which is indicated by the pressure in the eudiometer.

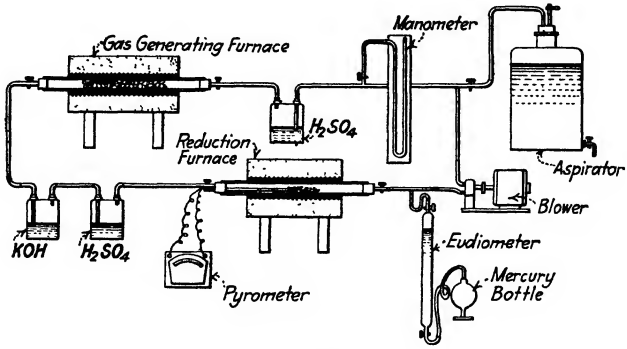

FIG. 5.

Some of the results of these experiments are as follows:

Number of Experiment	Weight of Sample, Grams	Time of Reduction		Analysis of Reduced Ore		Per Cent. of Reduction		Per Cent. of CO_2 in Gas at End of Reduction
		Hours	Minutes	Fe, Per Cent.	Total Fe, Per Cent.	By Analysis	By Weight	
27	20			80.598	88.021	91.6	91.4	9.4
28	30	5	10	78.831	82.719	95.3	92.4	4.7
41	80	3	45	88.900	94.971	93.6	90.75	4.9

In these experiments, fairly good results were obtained in spite of the fact that the ore was larger and in all cases the percentages of reduction were over 90 per cent. In experiment 28, the time of reduction was much longer than in experiment 41, with the quantity of the ore smaller. This is why the volume of CO gas passed in No. 28, in unit time, was much smaller than in No. 41.

Because quite good results in reduction of the ore, even with the size of the ore up to 4 mesh per linear inch, were obtained, the reduction was tried at 900° C. on larger sizes of Santo hematite, and the following results were obtained:

Number of Experiment	Weight of One Piece of Ore, Grams	Time of Reduction		Analysis of Reduced Sample			Per Cent. of Reduction		Per Cent. CO_2 in Gas at End of Rduction
		Hours	Minutes	Fe, Per Cent.	Total Fe, Per Cent.	C, Per Cent.	By Analysis	By Weight	
37a	2.5522								
37b	2.5261	1	10	95.091	96.505	0.859	98.5	99.4	3.3
37c	1.7961								
38a	2.9833								
38b	1.9900	1	35	95.798	96.909	0.369	98.8	98.4	1.6
38c	2.0167								
38d	2.0147								
39a	10.5536								
39b	8.1070	3	5					97.1	3.2

In experiments 37 and 38, one piece of ore weighed 2 to 3 gm. and time of reduction was 1 hr. 10 min. and 1 hr. 35 min., respectively, without measuring the volume of gas. The size of ore was about 1 cm. Even in such a piece, nearly perfect reduction was obtained in a very short time.

Fig. 6.

Therefore, in experiment 39, the two pieces of ore being about 10 and 8 gm. and about 2 cm. in size, the percentage of CO_2 of 3.2 in the gas after a reduction for 3 hr. makes the percentage of reduction 97.1 per cent. The percentage of CO_2 in reduction gas decreased gradually when the reduction progressed.

In these three experiments, when the percentage of CO_2 in the gas became about 3 per cent., the reduction attained was nearly perfect.

Fig. 6 shows the piece reduced in experiment 39a and Fig. 7 is the photomicrograph of the same sample polished, and shows the spongy structure of the reduced iron.

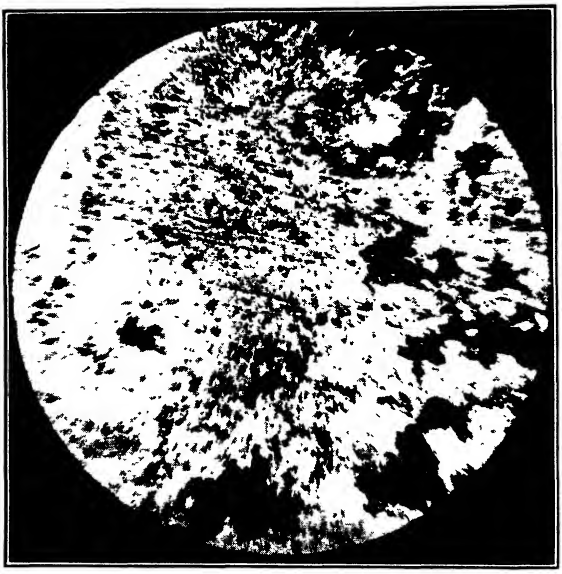

FIG. 7

RATE OF REDUCTION ON DIFFERENT KINDS OF ORE

There must be some difference in the rate of reduction, or reducibility, of different kinds of ores as all are of different natures, so seven kinds were used in this investigation. The ore was rather coarse as previous experiments had shown that there is not a marked difference in reducibility as to size up to a certain point. The ore was three to four mesh per linear inch, except the Sahinai magnetite which was four to eight mesh per linear inch, and the Wanisu magnetite sands. The analysis of the ore was as follows:

Kind of Ore	H_2O, Per Cent.	Ignition Loss, Per Cent.	Fe as Fe_3O_4, Per Cent.	Fe as FeO, Per Cent.	Fe as Fe_2O_3, Per Cent.	Total Fe, Per Cent.	SiO_2, Per Cent.	Al_2O_3, Per Cent.	CaO, Per Cent.	TiO_2, Per Cent.	Mn, Per Cent.	MgO, Per Cent.	P, Per Cent.	S, Per Cent.
Taihei limonite	0.38	12.60				55.29	4.94	5.02	0.60		1.38	0.15	0.94	1.07
Taiya hematite		4.25	4.52		55.12	59.64	5.50	2.70	0.49		0.29	0.35	0.04	0.12
Santo hematite	0.10	0.84				67.16	8.08	0.96	0.43		0.15	0.15	0.04	Trace
Tochu hematite		2.82	2.32		59.70	62.02	6.34	1.04	0.42		0.12	0.15	0.04	0.01
Sahinai magnetite			49.50		3.45	52.95	9.62	1.56	5.62			0.17	0.03	0.09
Rigen hematite			1.61		56.21	57.82	15.86	Trace	Trace			0.04	0.01	Trace
Wanisu magnetite sands				21.08		52.74	15.65			10.50				

The experiment of the reduction was made by the equipment shown in Fig. 5. The weight of the ore, taken in the tube, was 100 gm. and ores, like Taihei and Taiya, that contain some combined water were previously roasted. The typical results of reduction for each kind of ore are given in the accompanying table.

Number of Experiment	Kind of Ore	Weight of Reduced Sample, Grams	Time of Reduction		Volume CO Used, Liters	Velocity of CO Passed, C. C. per Min.	Per Cent. of Reduction		
			Hours	Minutes			By Weight	By M. Fe in Analysis	By O_2 Formed CO_2 with CO
87	Taihei..........	72.5300	3	15	173.660	890	96.4	95.0	95.0
73	Taiya	74.0056	4	0	173.870	725		88.8	93.6
88	Santo...........	70.1668	4	45	238.790	838		93.6	96.0
94	Tochu	71.6750	4	30	248.300	920	94.9	91.5	91.5
90	Sahinai.........	82.8500	4	55	199.361	676	78.8	73.7	85.9
89	Rigen..	78.4278	4	0	221.982	925	82.5	82.0	81.3
79	Wanisu magnetite sands (50 gm.) .	41.7065	5	0	109.816	732	90.5	75.5	75.1

With the Taihei, Taiya, Santo, and Tochu ores, a reduction to metallic state of over 90 per cent. was obtained by passing from 725 to 920

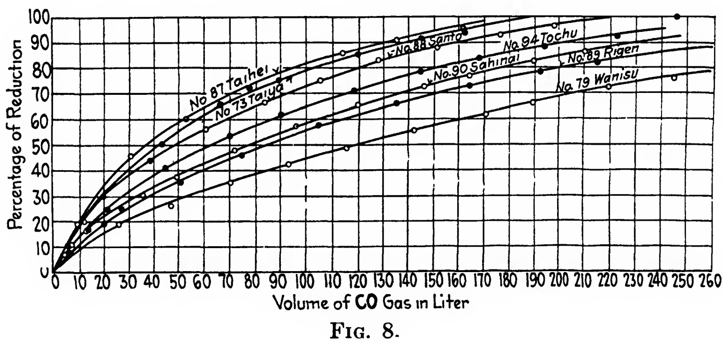

FIG. 8.

c. c. per min. of CO gas, but in the case of Sahinai, Rigen and Wanisu magnetite sands, the velocity of reduction was much slower. The percentages of reduction are calculated in three ways; and all the results nearly agree with each other, with the exception of Sahinai magnetite and Wanisu magnetic sands.

The curves in Fig. 8 are plotted, taking the volume of CO gas in standard condition as ordinates and the percentage of reduction as abscissas, to compare the reducibility of the seven kinds of ore. For this purpose it is necessary to keep the volume of gas constant for a certain unit of Fe content in the sample. It was not possible to keep the velocity of gas constant, but roughly so. To make the comparison more

accurate for different ores, in the curves, the volume of CO gas is calculated based on the one atomic gram of iron content (56 gm.) in each ore.

Relation of Reducibility and Density of Ore

The difference in reducibility of different ores is shown by the curves in Fig. 8. Taihei limonite is most easily reducible and the Wanisu

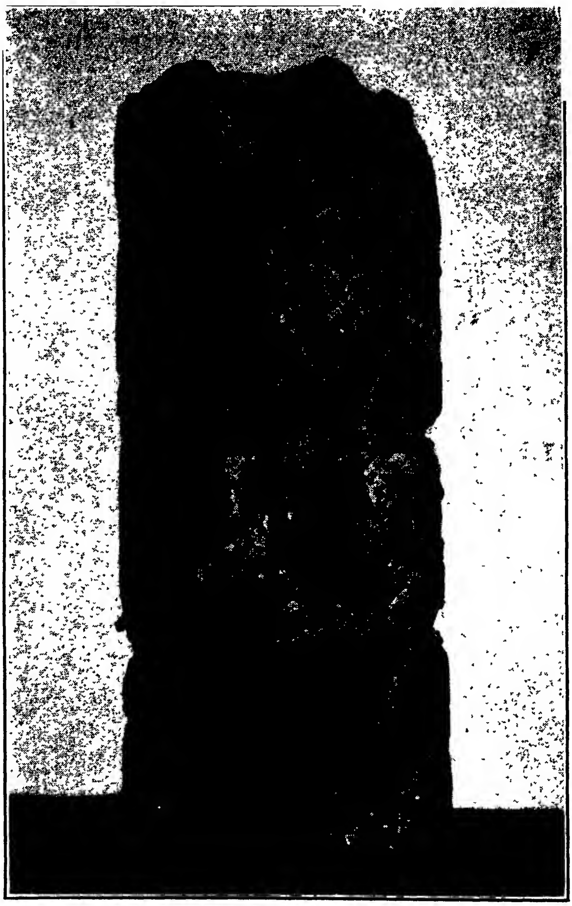

Fig. 9.

magnetite sands are most difficult to reduce. A reduced iron from Taihei limonite is shown in Fig. 9. This experiment was made on 100 gm. of ore in the combustion tube, the sample filling it about one-third of its diameter. After reduction, the tube was filled by a reduced spongy iron, by expansion as shown. Generally speaking, the ores expand more or less by the heating in reduction and they do not shrink to the previous size, owing to the combined oxygen with iron taken off during the reduc-

tion. In the case of limonite, the whole combined water with Fe_2O_3 dissociates during the heating, say 500° C., so that the heated ores assume a very porous state. As a result, the gases would diffuse into the ore very easily and the reducing action of the gas takes place more rapidly. This is the reason why Taihei limonite is easily reducible.

It was thought that the physical properties of the ore might have a large influence on the reducibility, that there must be some relation between reducibility and density of the ore for reduction in different kind of ores. The apparent specific gravity, therefore, was measured for the seven kinds of ores used in the experiments just described.

Kind of Ore	Fe Content, Per Cent.	TiO_2, Per Cent.	Apparent Specific Gravity	Real Specific Gravity
Taihei	55.29		3.25	3.956
Taiya	59.64		3.80	4.426
Tochu	62.02		4.38	4.492
Santo	67.55		4.53	4.743
Sahinai	52.95		4.56	4.616
Rigen	57.82		4.57	4.511
Wanisu	49.63	10.50		4.900

Comparing these specific gravities of the ores and their reducibility in the curves in Fig. 8 will show that the order of reducibility of ores nearly coincides with their specific gravity. The smaller the specific gravity, the more easily does the reducing action take place. The only exception is in the case of Santo ore, which has heavier specific gravity than Tochu ore, but its reduction is easier than the latter. This is why one does not take account of the iron content in the ore. Strictly speaking, we should compare the specific gravity of iron oxide in the ore, but it is impossible as the ore contains some gangue. If we assume that the specific gravity of the gangue, like SiO_2, Al_2O_3, $CaCO_3$, is 2.7, by calculation the specific gravity of the iron oxide in the ore will be as follows:

Kind of Ore	Fe Content, Per Cent.	As Fe Oxide, Per Cent.	$Fe_3O_4+TiO_2$	Gangue, Per Cent.	Apparent Specific Gravity
Taihei	55.29	78.99		21.01	3.42
Taiya	59.64	84.98		15.02	3.99
Tochu	62.02	88.54		11.46	4.60
Santo	67.55	96.46		3.54	4.60
Sahinai	52.95	73.29		26.71	5.23
Rigen	57.82	82.45		17.55	4.97
Wanisu	49.63		78.38	21.62	5.50

Here the specific gravities of Tochu and Santo ores are the same, but Santo ore is easier to reduce than Tochu. The reduction of Rigen hematite is very difficult, considering its specific gravity; this is probably due to the degree of crystallization. Comparing the specific gravity in the table and the reducibility, we can say that there is a definite relation between specific gravity and reducibility; also, that the higher the degree of crystallization of the ore the more difficult the reduction will be.

Size of Ore for Reduction

As fairly good results were obtained in from 3 to 5 hr., in the reduction of ore up to 3-mesh, further experiments were made to find the maximum size of ore allowable for reduction in a certain time. It is difficult to express the size of the lump ore by length, so it is designated by weight.

Number of Experiment	Kind of Ore	Weight of Ore, Grams	Time of Reduction		Velocity of CO Gas, C. C. per Min.	Weight of Reduced Iron, Grams	Per Cent. of Reduction Calculated by Weight
			Hours	Minutes			
70a	Taiya..............	41.4165				29.3000	97.9
70b	Tochu..............	43.2600	7	00		31.5400	87.4
83	Tochu 2 pieces......	69.2150	5	15	798	49.4490	95.5
84	Taiya 3 pieces.......	91.6981	4	55	780	65.5035	93.9
85	Taiya 1 piece.......	42.3030	3	45	1134	30.7890	87.5
86	Taiya 3 pieces.......	106.3227	3	20	1021	76.3293	91.8
94	Taiya 1 piece.......	39.3028	1	30	2720	28.3921	89.3

The velocity of gas was calculated on the basis of 100 gm. of ore. In experiment 70a, the sample placed at the inlet side of the gas was nearly

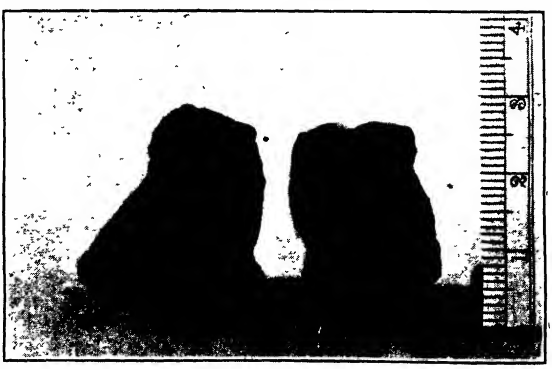

Fig. 10.

reduced. In No. 83, two pieces of Tochu ore were reduced during the 5 hr. with a gas velocity of 798 c. c. per min. and 95.5 per cent. of reduc-

tion was obtained. In No. 94, the gas velocity was increased to 2720 c. c. per min. and in 1½ hr. 89.3 per cent. of reduction was obtained. Fig. 10 shows a piece of reduced iron from experiment 83 that was broken into two pieces. A dark spot, in the center, shows that some unreduced FeO still exists.

Conclusions

From this investigation, the following conclusions were drawn:

1. The proper temperature for reduction of iron ores by carbon monoxide gas depends on the physical properties and the chemical composition of the ore. In the case of limonite or hematite, it is about 900° C.; in the case of magnetite or magnetite sands, slightly higher temperatures are needed.

2. The difference in reducibility of the ores depends mostly on their physical properties. The denser the ore, the more difficult is the reducing action of gas as the diffusion of gas will be slower; generally, the density of an ore will indicate its reducibility. The degree of crystallization of the ore, also, has much influence on the reducibility.

3. The time for reduction will be determined by reducibility, size of ore, and volume of CO gas passed. In these experiments, nearly perfect reduction was obtained in from 2 to 3 hr. on the 1-cm. size of ore, using the proper volume of gas.

4. The finer the ore, the easier the reduction, but it is better that the ore have some size to a certain extent as the gas diffuses easily between the particles of the ore. In the experiments, reduction was tried on the ore up to 40-gm. pieces (1 by 1½ in.). The time required for the reduction was from 3½ to 5 hr. in the 1-in. size of ore, and from 2 to 3 hr. for ore under ½ in. in size.

The blast furnace is pre-eminently the most economic iron producer today and its degree of efficiency has probably reached the highest point of development. Probably few devices have so closely approached the perfection of which, by their nature, they are capable. Fifty years ago nearly thrice as much fuel was often used as is needed today in the best blast furnaces. Nevertheless, blast-furnace operation is open to grave criticism. The iron is not only brought to the metallic state, which can be done at a low temperature as in these experiments, but the deoxidized iron is raised to a much higher temperature. This high temperature causes such strong deoxidation that other metallic and non-metallic compounds in the ore are reduced, the resultant iron being marked by impurities, such as phosphorus, silicon, manganese, carbon, etc.; also much more heat energy is needed for the operation. This also necessitates secondary treatment in converters and open-hearth furnaces to remove impurities for refined steel. This procedure of making steel by carburizing iron in the blast furnace and then decarburizing it is illogical.

If the iron ores are reduced to the metallic state at about 900° C. by CO gas, as in these experiments, and the resulting spongy iron, without cooling, is melted down in electric furnaces, the steel may be made directly from the ore. The calculations made in this paper show that the theoretical heat energy in this process is only one-half the theoretical heat required in the blast furnace. Assuming the same thermal efficiency in the two cases, in this process 0.5 ton of coal as fuel and 500 kw.-hr. for melting 1 ton of steel will be sufficient instead of 1 ton of coke per ton of pig iron in the blast furnace.

It is reasonable to conclude that any process aiming at the production of iron or steel direct from the ore must take into account considerations that are of such great importance in iron metallurgy; viz., time and temperature of reduction and strength of reducing agent.

Many proposals have been made for solving the direct-reduction process. But it is fallacious to reason that the process will not succeed because, in the past, usually ill-advised attempts have failed, have wasted much iron and more gold, and have used more fuel than the blast furnace—because the direct process in its infancy was weaker than the blast furnace in its perfection. The experimenters failed because they did not overcome obstacles, often unseen, not understood, serious, but not in their nature insuperable; they failed not because the direct process lacked capability but because it was difficult.

To apply those fundamental principles determined in this research work for the development of the direct process demands a high degree of metallurgical and engineering talent and knowledge, and, just for lack of these, the direct process has failed in the past. But today our knowledge is greater and the amount of trained talent available for solving difficult metallurgical problems is incomparably greater than formerly, and both knowledge and the quantity of available talent are increasing rapidly.

Acknowledgment

This research was carried on in the Metallurgical Laboratory of Meiji College of Technology. The author wishes to express his appreciation of the courtesy of President Oba and Professor Nakagawa, who gave most helpful advice regarding this work.

DISCUSSION

T. L. Joseph,* Minneapolis, Minn.—In his experiments, the author placed the iron ore in a small alundum boat, which was placed in an electric-resistance furnace, and the gases were passed over the small boat. By this arrangement there is not the contact between the gas and the

* Metallurgist, Bureau of Mines.

ore that would be obtained under conditions where the gas is forced through the ore.

A number of years ago Doctor Eastman performed a series of experiments very similar to those performed by the author; he used a 1-in. pipe as a container, the pipe being in a horizontal position and rotated at a very low speed. Doctor Eastman found that there was very little difference in the rate of reduction as he increased the depth of charge in the tube until the tube was entirely filled with ore, when the gas was forced through the ore and not over the top surface; under such conditions the rate of reduction almost doubled. As a result, I cannot agree with some of the conclusions in this paper. For example, the author concluded that the size of ore particles had very little effect on the rate of reduction; Doctor Eastman found quite the opposite. In his series of experiments he obtained data that led him to believe that the size of ore particles had a marked effect on the rate of reduction.

There seems to be a slight inconsistency in the paper. On page 555, it states that there is no evidence in the curves that the size of ore has any influence on the velocity of reduction, while at the end of the paper one of the conclusions is that the finer the ore, the easier the reduction. It is also stated, however, that the ore should have some size in order that the gases may diffuse easily between the particles of the ore.

R. Franchot,* Washington, D. C.—It is stated among the conclusions that the theoretical heat energy required in the process is only half the theoretical heat required in the blast furnace. This immediately raises the question: What is the theoretical fuel requirement in the blast furnace? Again, in the presentation of the paper it was stated that less carbon is required to reduce iron ore with carbon "directly," as it was expressed, than with carbon monoxide. These statements may be seriously questioned.

The latter statement seems to be based solely on the chemical equations on the first page of the paper; it may be pointed out that these equations take no account of the heat relations. According to Richards, the dissociation of hematite involves an absorption of 1746 calories per unit of iron. If the reduction takes place with conversion of solid carbon to CO_2, the oxidation of 0.16 units of carbon per unit of iron supplies 1296 calories, leaving 450 calories per unit of iron to be otherwise supplied. The deficit of heat per pound iron is equivalent to 0.18 lb. carbon with cold air, or 0.14 lb. carbon with the usual hot blast, burning to CO under blast-furnace conditions.

On the other hand, the reduction of hematite by CO with formation of CO_2, although it requires 0.32 lb. carbon as CO, is exothermic, the oxidation heat being 1814 calories against 1746 calories absorbed. If the CO

* Vice-president, Ferro-Chemicals, Inc.

is formed from cold air, the heat developed thereby is 777 calories per unit of iron; and with hot blast, 1024 calories, this heat of CO formation being available for melting iron and slag, calcining limestone, etc. With a usual slag ratio of 50 and 45 per cent. stone, the purely heating work may be estimated at about 800 calories per unit iron, and it appears that the heat of formation of the CO required for reduction is equal to the heat absorbed in the work other than reduction. From a broad point of view, therefore, it appears that the theoretical fuel requirement in the blast furnace may be taken to be about 1/3 lb. of carbon per pound of iron, assuming reduction by CO and about twice this figure if reduction is to be effected by the so-called "direct" oxidation of carbon to CO_2.

Ralph H. Sweetser,* Columbus, Ohio.—I agree with the statement that it is a waste to use fuel to put carbon into pig iron, and then use more fuel in the open hearth to take the carbon out. There has been no authoritative statement as to how much fuel it takes to make a ton of pig iron, nor as to how much carbon there should be in pig iron.

No one has yet given a satisfactory answer to the question, how much carbon do open-hearth men want in the pig iron used in making open-hearth steel? If an open-hearth man is asked how much carbon he wants, he will say, "The usual amount." He will tell you exactly how much silicon, phosphorus, and manganese he wants and he will say that he does not want any sulfur at all; but he does not seem to know how much carbon he wants.

C. H. Herty, Jr.,† Lackawanna, N. Y.—The amount of carbon an open-hearth man wants in the pig iron depends on three or four factors. First, the ratio of scrap to pig he is going to use; second, the amount of silicon, phosphorus, and sulfur in pig iron along with the carbon. For instance, with very little silicon and high phosphorus and high sulfur, high carbon is desired because when the pig melts down the silicon is taken out of it. If the pig is low in carbon, the phosphorus may not be removed because the excess iron oxide over that required to take care of the silicon is going to attack carbon, and you are going to melt low in carbon. On the other hand, with high silicon and low phosphorus and low sulfur, the pig iron can have much lower carbon; silicon takes most of the iron oxide and the low phosphorus and low sulfur do not need it for their elimination. The impurities in the pig iron and the type of process being worked as much as anything must also be taken into consideration.

Ralph H. Sweetser.—With high sulfur and low phosphorus you do not want much carbon.

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* Assistant to Vice-president, American Rolling Mill Co.

† Research Associate, Massachusetts Institute of Technology, School of Chemical Engineering Practice.

C. H. Herty, Jr.—For a given silicon content of the iron, with high sulfur and high phosphorus you want high carbon; with low sulfur and low phosphorus, just the opposite. With either one low and the other high, you want to strike a mean between low and high carbon.

H. Kamura (author's reply to discussion).—As to the statement of Mr. Joseph concerning the effect of the size of ore on the rate of reduction, I would say that there should be a marked difference in the rate if you compare the rate between fines and lumps; but in the case of small differences in size, as between 30 and 40 meshes per linear inch, the size of the ore particles will have very little effect on the rate of reduction. Of course, it is necessary in this comparison to use the same volume of the gas for reduction per unit weight of iron content in the ore.

As to the theoretical fuel requirement in the blast furnace; that is, the theoretical amount of heat required in the blast furnace, I would say there is no definite amount of heat required per ton of pig iron produced. The amount is dependent solely on the condition of the blast furnace itself; *viz.*, composition of the ore used, composition of pig iron made, and all the conditions of working, etc. But we can say, in the usual working of the modern blast furnace using the ores that contains about 50 per cent. of Fe, the heat value in the fuel charged in the furnace will run from 3,300,000 to 3,500,000 calories per metric ton of pig iron, according to the heat balance of the blast furnace. From this basis, the theoretical requirement of heat in the process that I have calculated will be about half the heat required in the blast furnace. I admit that the amount of carbon required to reduce iron oxide with carbon "directly" will be less than with carbon monoxide, not only as based on the chemical equations but as based on the heat relations in two thermal equations:

1. Reduction with carbon,

$$\underset{-391{,}200}{2Fe_2O_3} + 3C = 4Fe + \underset{-291{,}600}{3CO_2} - 450 \text{ cal. per kg. of iron}$$

$$-99{,}600$$

This 450 cal. deficit corresponds to 0.055 kg. of carbon to burn CO_2. Assuming that the iron is reduced by the above equation, the theoretical amount of carbon required for reduction will be,

$$0.16 + 0.055 = 0.215 \text{ kg. of carbon per kg. of iron.}$$

2. Reduction with carbon monoxide.

$$\underset{-195{,}600}{Fe_2O_3 + 3CO} = 2Fe + \underset{-204{,}120}{3CO_2} - 76 \text{ cal. per kg. of iron.}$$

$$-8{,}520$$

This development of heat is equivalent to 0.013 kg. of carbon in CO to form CO_2, so that, in this case, the weight of carbon required $0.320 - 0.013 = 0.307$ kg. of carbon per kg. of iron. It does not matter whether the heat developed to form CO is utilized or not.

Austenite and Austenitic Steels*

By John A. Mathews,† Ph.D., Sc.D., New York, N. Y.

It is a great honor to be asked by the Board of Directors of this Institute to deliver the Henry Marion Howe lecture. The invitation carries with it a great responsibility, which I accept with considerable hesitation and with a feeling of unworthiness to perform the duties expected of me in this hour devoted to the memory of the life, character, and work of the late Professor Howe. Many of you recall the scholarly address delivered here a year ago by Prof. Albert Sauveur, and the beautiful tribute he paid to his friend and colleague of many years in the great work of changing the art of iron making into the science of iron.

My association with Professor Howe was of brief duration—only one year—and the relation was that of pupil to teacher. My feeling toward him in later years was always that of a humble disciple at the feet of a master. He attained his third academic degree in the year that I was born. I recall the pride I felt when, after entering the steel industry, I received from him, from time to time, letters asking for information or, perchance, asking my opinion, and he was always most punctilious in acknowledging the source of such bits of information in his writings.

It was also my good fortune to sit at the feet of another great teacher—Sir William Roberts-Austen, at the Royal School of Mines. I mention him because his name was used by Osmond in coining the word "austenite," which is the subject of this address, and Osmond's suggestion was heartily approved by Howe. These three international metallurgists were the best of friends and delighted to honor the achievements of one another. There are other reasons for mentioning Roberts-Austen at this time. It was an introduction from Howe that opened to me the door of his laboratory as well as of his heart. It was while at Roberts-Austen's laboratory that I worked side by side with William Campbell

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* Second Annual Henry Marion Howe Memorial Lecture, delivered at the New York Meeting of the American Institute of Mining and Metallurgical Engineers, February 16, 1925.

† Vice-President, Crucible Steel Co. of America.

for a year and I have always taken credit for having stimulated his interest in Howe and of interesting Howe in Campbell, with the result that Campbell entered Columbia University in 1901 and now has the honor of filling the Henry M. Howe Professorship of Metallurgy, a chair named in honor of his illustrious predecessor.

When a student under both Roberts-Austen and Howe, I frequently felt that I was not receiving enough of their personal time and attention; in fact, I felt that they neglected me. But on looking back twenty-five years I realize that it was inspiration and not information that I received from my contacts with them—not so much from routine lectures as from personal observation of the men and their methods, their personalities and ideals. They made a lasting impression upon me and influenced my life and activities more than any other teachers during my years of collegiate and university training.

Part I. Austenitic Steels

One of the earliest of all commercial alloy steels was Hadfield's manganese steel; this steel is a typical austenitic steel. It early attracted the attention of Professor Howe and he was for many years interested in it, both scientifically and commercially. Several of his scientific papers deal with it and he took out a patent in connection with its manufacture. The anomalous properties of this steel attracted wide attention for many years after its discovery and it furnished a fruitful field for investigation before its constitution was understood. It is not my intention to discuss this important industrial product on this occasion, but merely to refer to Howe's connection with both its manufacture and investigation. His nephew, John Howe Hall, has recently written an interesting and instructive paper on the subject of manganese steel, to which you are referred.[1]

All enlightened, tool-using people, with a smattering of technical or mechanical training, have some definite ideas about steel and some knowledge of its properties. They know it is a heavy metal and that it rusts; that it is attracted by the magnet; that it is capable of greatly increased hardness by plunging into water at a red heat; that overheating causes heavy scaling and cracking upon quenching. They know that in the hardened state it becomes permanently magnetized. Every schoolboy likes to have his knife blade magnetized. In days when men shaved with old-fashioned straight-edged razors, they took great pride in their keen edges. They were as proud of their razors as were the knights of old of their trusty swords. Imagine anyone waxing enthusiastic over an evanescent safety blade—here today and gone tomorrow.

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[1] John H. Hall and G. R. Hanks: Composition and Physical Properties of Cast 12 Per Cent. Manganese Steel. *Proc.* A. S. T. M. (1924) **24**, 626.

Robert Hooke, the discoverer of Hooke's Law and an early Secretary of the Royal Society, was the first to attempt to picture what the microscope revealed; at least as regards steel. He published his Micrographia in 1665 and the book is filled with beautiful engravings of natural history or biological objects, with the exception of one of the first illustrations. Hooke could not resist the temptation to show the public what a razor edge looks like under magnification. A copy of this book is one of my prized possessions.

Most of this fundamental information about steel is of great antiquity as shown by classic writers. In short, the public—past and present—knew or knows something of alpha-iron metallurgy. The public does not appreciate that there are many steel alloys which do not rust and, in fact, will resist many of the strongest acids, weak or strong solutions, and hot or cold. Many of these alloy steels are totally non-magnetic; they are greatly softened by quenching and are almost incapable of overheating short of fusion. They are not subject to heavy scaling and many of them will withstand 2000° F. for a long period in an oxidizing atmosphere. Ordinary steel is embrittled at low temperatures but some of these products become increasingly more resistant to shock as the temperature decreases, as shown by Langenberg's exhaustive investigations at temperatures as low as −80° F. We have immersed some of these alloys in liquid air and, after 15 min. refrigeration, found them to flow readily under hammering and to stand a flat cold bend.

This is not general knowledge; in fact, it is not widely known to steel metallurgists and engineers. It is gamma-iron metallurgy. The very great industrial usefulness of alloys possessing such remarkable properties seems to warrant some consideration of their physical properties and structures. Gamma-iron metallurgy is in the making. We shall know better how to use these steels when we understand their metallurgy and properties. I hope my contribution may arouse a more general interest in them and more particularly in a study of gamma iron. They have had much attention in certain directions for almost a generation but they cannot be said to be generally understood or appreciated from an engineering point of view.

The steels to which I particularly refer include, first, the very high nickel steels, sometimes called ferro-nickels, containing from 25 per cent. of nickel upward. They have been most studied by Guillaume and other French metallurgists. While they possess considerable resistance to corrosion and have been used for non-corrosive requirements, their most interesting physical properties are those due to various coefficients of expansion from almost zero to values duplicating those of platinum, glass, etc. The use of these as boiler tubes was extensively investigated over 20 years ago.

Second, the high-chromium steels, which are due principally to the investigations of Brearley, Haynes and Becket. The ones that have found industrial application vary from 8 to 30 per cent. The group from 20 to 30 per cent. has been described by MacQuigg[2] before this Institute, and also before the American Society of Testing Materials.[3] We also recall Monypenny's[4] paper on stainless iron, delivered here a year ago.

Third, the high-chromium nickel steels, particularly those of B. Strauss, in which the chromium is usually much higher than the nickel. They were described by him in a paper before the American Society for Testing Materials in 1924.

Fourth, the high-chromium nickel steels, in which nickel is usually higher than the chromium and to which a substantial amount of silicon is added, say from 2 to 3½ per cent. Considering the low atomic weight of silicon, this is a very high addition, when atomic concentration is considered. This group is due to C. M. Johnson,[5] and were described by him in 1921.

It seemed to me that a comparison of the physical properties of a series of steels varying between 30 per cent. nickel and 30 per cent. chromium might be interesting and enlightening. In the chromium-nickel members of this series, the total of these two elements is approximately 30 per cent. The steels referred to are given in Table 1.

Table 1

Mark	Carbon, Per Cent.	Chromium, Per Cent.	Nickel, Per Cent.	Silicon, Per Cent.	Manganese, Per Cent.
C-30-0	0.30	29.77		0.67	0.56
C-25-0	0.33	24.58		0.63	0.30
CN-21-7	0.32	20.73	7.04	0.65	0.27
CN-15-15	0 39	15.35	15.60	2.26	0.82
CN-7-22	0.41	7.29	22.60	1.84	0.80
N-0-28	0.43		28.28	0.25	0.73
N-0-30	0.12		30.25	0.14	0.37

It will be noted that the scheme of marking gives an approximate idea of composition. Two plain chromium steels are included and for the first of these I am indebted to F. M. Becket. They are so nearly alike except for chromium content that their differences due to that element may be closely studied. The two high-nickel steels were included to show something of the influence of carbon in high-nickel steels. Most com-

[2] C. E. MacQuigg: Some Commercial Alloys of Iron, Chromium and Carbon in the Higher Chromium Ranges. *Trans.* (1923) **69**, 831.

[3] C. E. MacQuigg: Some Engineering Applications of High Chromium-iron Alloy. *Proc.* A. S. T. M. (1924) **24**, 373.

[4] J. H. G. Monypenny: Stainless Steel, with Particular Reference to the Milder Varieties. *Trans.* (1924) **70**, 47.

[5] C. M. Johnson: Properties and Microstructure of Heat-treated Non-magnetic, Flame-, Acids-, and Rust-resisting Steel. *Trans.* A. S. S. T. (1920), **1**, 554.

plete tests, however, were made on the five intermediate members of the series.

This interesting group of alloys, all of which represent commercial types of steel, are usually considered as austenitic in character. However, only the three chrome-nickel steels belong strictly to that category. This series of steels was subjected to various physical tests, to be described later, including Rockwell and Brinell hardness, specific resistance, magnetic, thermal-expansion and microscopic. They were also tested for resistance to oxidation or scaling at high temperatures. The types they individually represent have been exhaustively studied as to corrosion by the author and others, and this feature will not be emphasized here.

The tests were made in the natural, or as-rolled, condition; after normalizing at 1600° F., holding at heat for 5 min. followed by natural cooling in air; after annealing between 1350° and 1400° F., holding at temperature for 2 hr., followed by very slow cooling at about the rate of 50° F. in 2 hr.; after quenching in oil from a temperature of 2200° F., after holding at heat for 5 min., and, finally, after such quenching they were reheated or drawn at 1400° F. Other hardening and drawing temperatures were also tried, such as 1600° and 1900° F. quenching and 500°, 800°, and 1100° F. drawing, but these revealed nothing of special interest and will be omitted. It is interesting to note that the highest quenching temperature in no case produced cracking and in this they are decidedly different from ordinary steels quenched at such a temperature. The reason for selecting 2200° F. was to give the greatest opportunity for the solution of carbides or other compounds and to insure the greatest possibility of producing fully austenized steels.

Hardness

Only a small amount of the C-30-0 steel was available and hardness tests were not made on it. Steel C-25-0 is the only one of the series which showed any capacity at all for hardening by quenching, and it increased only from 187 Brinell, natural, to 207, quenched. Taking the series as a whole C-21-7 was hardest in all conditions and its natural hardness of 302 was not lessened by normalizing or annealing. All the steels, except C-25-0, were materially softened by quenching and all of them, without exception, showed slightly greater Brinell hardness after quenching and drawing at 1400° F. than in the as-quenched state. The three quarternary alloys are naturally harder than the ternary ones. The Rockwell hardness tests check the Brinell tests with a few exceptions and the details of all hardness tests are given in Table 2.

While these alloys do not harden greatly by quenching and more frequently are softened by this treatment, it must not be supposed that the influence of carbon is negligible. Increasing the carbon increases the

hardness in the natural state and raises the tensile strength and yield point and reduces the elongation and reduction. It also makes them harder and more difficult to forge at high temperatures.

All of these steels may be forged, rolled, cold drawn, or cold rolled; they are suitable for cold forming operations and may also be drop forged in dies. The available range of heating is somewhat narrow and must be controlled closely in hot working. Being fairly hard at a red-heat, they do not flow as readily in forging as ordinary carbon or alloy steels.

TABLE 2.—*Hardness and Specific Resistance*

Mark	C-30-0	C-25-0	CN-21-7	CN-15-15	CN-7-22	N-0-28	N-0-30
Carbon, per cent	0.30	0.33	0.32	0.39	0.41	0.43	0.12
Chromium, per cent	29.77	24.58	20.73	15.35	7.29		
Nickel, per cent			7.04	15.60	22 60	28.28	30.25
Brinell, as rolled		187	302	235	228	174	143
Normalized at 1600° F.		183	302	207	166	153	112
Annealed at 1400° F.		179	302	196	163	131	114
Quenched at 2200° F. in oil		207	234	192	163	140	114
Quenched and drawn at 1400° F.		212	286	196	179	149	118
Rockwell (B scale) as rolled		91	104	99	98	84	77
Normalized		89	104	94	84	73	61
Annealed		89	105	90	84	70	63
Quenched		96	98	93	87	71	61
Quenched and drawn		96	100	90	88	73	66
Specific resistance (micro-ohms per c c.) as rolled	69.4	68.5	77.6	91.1	92.7	86	85
Normalized	69.4	68.5	76.4	91.1	92.7	86	85
Annealed		68.5	75.2	89.9	92.7	86	85
Quenched	71.9	72.1	76.9	93.0	94.9	88.4	86
Quenched and drawn	70.5	69.7	76.9	91.3	93.3	86.2	83.8

Specific Resistance

Specific resistance is also included in Table 2 and is reported in terms of micro-ohms per cubic centimeter at 100° F. In general, the small changes for the widely different heat treatments are noteworthy. As between the two chrome steels, C-30-0 is but slightly higher in all conditions, except as quenched, notwithstanding it contains 5 per cent. more chromium, presumably in solution as chrome-ferrite. In explanation, we would suggest that chrome-ferrite is a very poor solvent for carbides, whether simple or complex, and for this reason in the two steels, as quenched, we find a slightly higher resistivity in the lower alloy, indicating that the carbides have gone into solution more fully; and after tempering a greater precipitation has occurred in this steel, again reducing its resistance below that of C-30-0.

The resistance of the chrome-nickel steels is notably higher than that of the chromium steels, but in the case of CN-15-15 and CN-7-22 this is doubtless due to their high-silicon content. These materials would

appear to be excellent resistance alloys. Steels of the type N-0-30 have been used for many years for this purpose but they are considerably lower in resistance than two of the chrome-nickel series. It will be noted that N-0-28 is slightly more resistant than N-0-30, indicating that the difference in carbon more than offsets the 2 per cent. difference in nickel.

Magnetic Properties

This portion of the test is considerably simplified by the fact that the three chrome-nickel members have no magnetic properties. They are practically non-magnetic in every condition of heat treatment. CN-15-15 was further tested to see if it became magnetic by stressing beyond its yield point; the result was negative.

As to the magnetic test of the ternary members of the series, we see some very interesting things. The chromium members, which contain 25 to 30 per cent. of non-magnetic chromium, show a much higher induction than the nickel steels containing 28 to 30 per cent. of magnetic nickel. Considering the high induction of the chrome steels, we must admit the presence of much alpha iron, even in the quenched state, yet the permeability and residual density are quite low after quenching, indicating a fairly successful effort at bringing about the austenitic state by a drastic cooling from a high temperature. While it appears that the coercive force has been increased by drawing the temper to 1400° F., if we consider the ratio of Br to Hc, we will see that the steel C-25-0 has really been magnetically softened by this treatment.

TABLE 3.—*Magnetic Properties*

Mark	C-30-0	C-25-0	CN-21-7	CN-15-15	CN-7-22	N-0-28	N-0-30
B max. (H-150) (maximum induction) as rolled..........	9,000	12,450	Practically non-magnetic			3,150	4,650
Normalized at 1600° F		12,750				2,250	3,750
Annealed at 1400° F.........		12,750				1,200	4,800
Quenched at 2200° F........	10,650	5,550				2,100	4,200
Quenched and drawn at 1400° F	12,000	12,450				1,200	4,800
B res. (residual density) as rolled	2,610	5,620				850	1,230
Normalized.................	3,300	4,370				113	447
Annealed....................		5,420				0	1,010
Quenched....................	2,850	728				113	624
Quenched and drawn.........	4,540	5,720				0	964
H coer. (coercive force) as rolled	2.35	4.6				1 35	1.5
Normalized.................	2.45	5.4				1	1
Annealed....................		4.6				0	1
Quenched....................	6.3	8.2				1	1
Quenched and drawn.........	5.75	11.4				0	1
μ max. (permeability) as rolled.	595	546				565	497
Normalized.................	683	479				510	559
Annealed....................		664				85	840
Quenched....................	238	68				283	565
Quenched and drawn.........	404	312				85	796

The low induction of the nickel steels would seem to indicate a considerable amount of gamma iron in all conditions and it is interesting to note that in N-0-28 the minimum induction (B) results either from annealing or by drawing after quenching, while in N-0-30 the maximum induction results from these treatments. The residual induction and coercive force are very low or lacking in both steels, yet in low fields for most conditions of treatment they show a fairly high permeability. The details are set forth in Table 3.

Coefficient of Expansion

Through the coöperation of the Bureau of Standards and its generous assistance in pushing through the testing of these alloy steels, I am able to present data on the coefficient of expansion that might not have been available at this time except for this assistance in the preparation for this occasion. Five alloys were tested in each of two conditions: (*a*) as normalized at 1600° F. and (*b*) after water quenching from 2000° F. The results are shown in Table 4.

TABLE 4.—*Average Coefficient of Expansion per Degree C.*

	20° TO 200° C.	20° TO 400° C.	20° TO 600° C.
C-25-0, normalized	0.0000164	0.0000172	0.0000176
C-25-0, quenched	0 0000165	0.0000172	0.0000177
CN-21-7, normalized	0.0000103	0.0000110	0.0000114
CN-21-7, quenched	0.0000117	0.0000124	0.0000122
CN-15-15, normalized	0.0000163	0.0000172	0.0000176
CN-15-15, quenched	0 0000164	0.0000175	0.0000178
CN-7-22, normalized	0.0000176	0.0000180	0.0000182
CN-7-22, quenched	0.0000177	0.0000181	0.0000182
N-0-28, normalized	0.0000138	0.0000161	0.0000163
N-0-28, quenched	0.0000138	0.0000161	0.0000165

It will be noticed that CN-21-7, which was the only steel that showed any capacity at all for hardening by quenching, shows greatest differences between the normalized and quenched states for the various ranges. The steel N-0-28 shows greatest increase in expansion over the three ranges.

Microscopic

This series of alloys was examined microscopically in the normalized and quenched states. I will only give a general résumé of this examination. Passing from the chromium end toward the nickel end, it is seen that grain size increases and also grain growth at high temperatures. The presence of carbides decreases as the chromium decreases and in

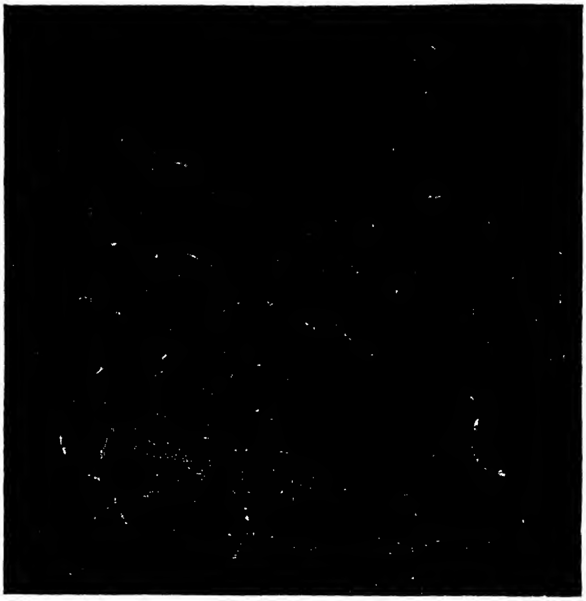

FIG. 1.—INGOT STRUCTURE, SHOWING MARKED DENDRITIC PATTERN. ×300

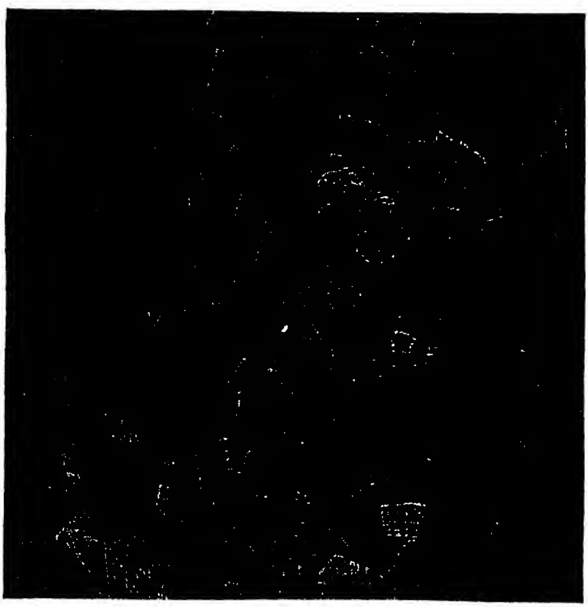

FIG. 2.—FORGED BAR FROM INGOT SHOWN IN FIG. 1; IT HAS HAD A LOW TEMPERATURE ANNEALING AND WAS QUENCHED FROM 950° F.; THE DENDRITIC STRUCTURE IS GONE. × 300.

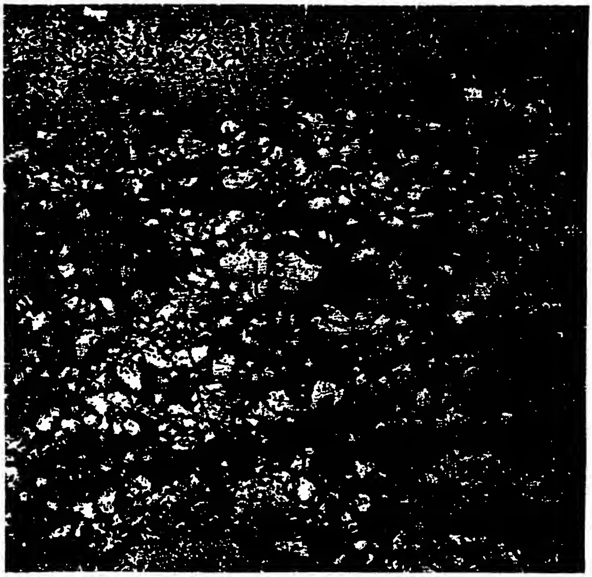

FIG. 3.—FORGED BAR SHOWN IN FIG. 2 AFTER IT HAD BEEN HELD AT 2000° F. FOR 1 HR. AND QUENCHED; DENDRITIC PATTERN IS NOT EVIDENT. × 300.

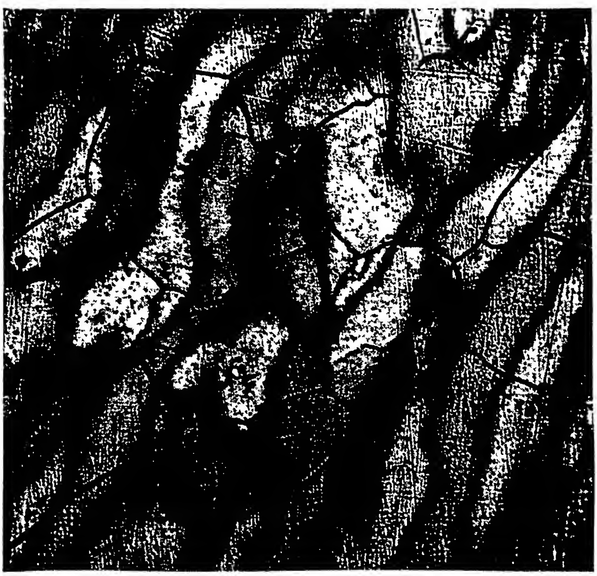

FIG. 4.—SAME BAR AFTER IT HAD BEEN HELD AT 2300° F. FOR 5 MIN. AND QUENCHED; NOTE RETURN OF SHADOWY DENDRITIC PATTERN PASSING THROUGH GRAIN BOUNDARIES. × 300.

C-25-0 and CN-22-7 these carbides appear largely at the grain boundaries and to some extent in streaks, passing through several grains. The polygonal grains are of more irregular formation in these steels and tend to become angular at the nickel end of the series. I am not certain that any true carbides are visible in the high-nickel steels. This is worthy of note, that nickel which has little affinity for carbon, which tends to precipitate it as graphite in high-carbon steels and to a certain extent retards carburizing processes in the ordinary 3½ and 5 per cent. nickel steels, seems to carry all its carbon in solution when present in high amounts. Chromium, on the other hand, has a great avidity for carbon and forms one or more simple or complex carbides; it prevents the precipitation of graphite and facilitates carburizing, yet large percentages seem to form

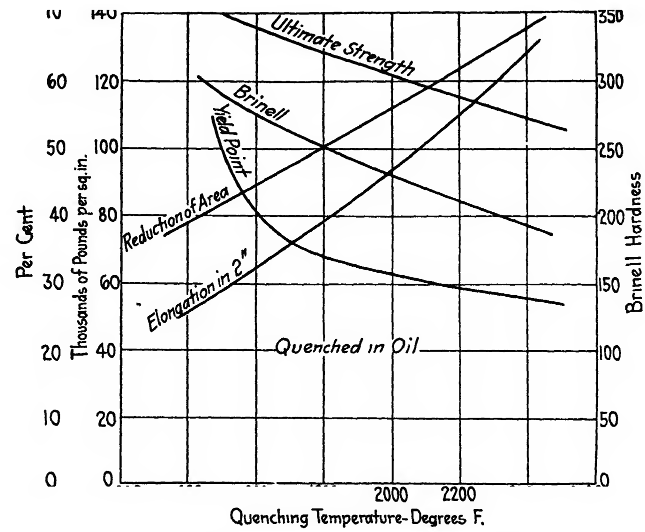

FIG. 5.—PHYSICAL PROPERTIES OF CN-15-15 TYPE ALLOY.

carbides so far as possible and the excess forms a solid solution of chrome-ferrite in which the carbides are very insoluble even at high temperatures. These steels, being naturally non-corrosive, are difficult to etch, and aqua regia is, in general, the most suitable reagent, although acid ferric chloride and Kourbatoff's solution work well with some of them.

I am not going to show the ordinary photomicrographs but have two series to present. First, there are four views to illustrate the persistence of the dendritic pattern; these are by C. M. Johnson and represent a steel similar to CN-15-15, but not the actual steel referred to in Tables 1, 2, and 3.

I referred earlier in this address to the anomalous behavior of these austenitic steels upon quenching. The curves, Fig. 5, represent the results of quenching in oil from ascending temperatures, from 1400° F. to 2500° F.

Elongation and reduction constantly increase until they reach very high values. Ultimate strength, yield point and hardness decrease. These steels were not reheated after hardening. Impact tests were not shown because they were not made with the standard test piece; however, with a light Izod machine and very deeply notched specimens, they showed

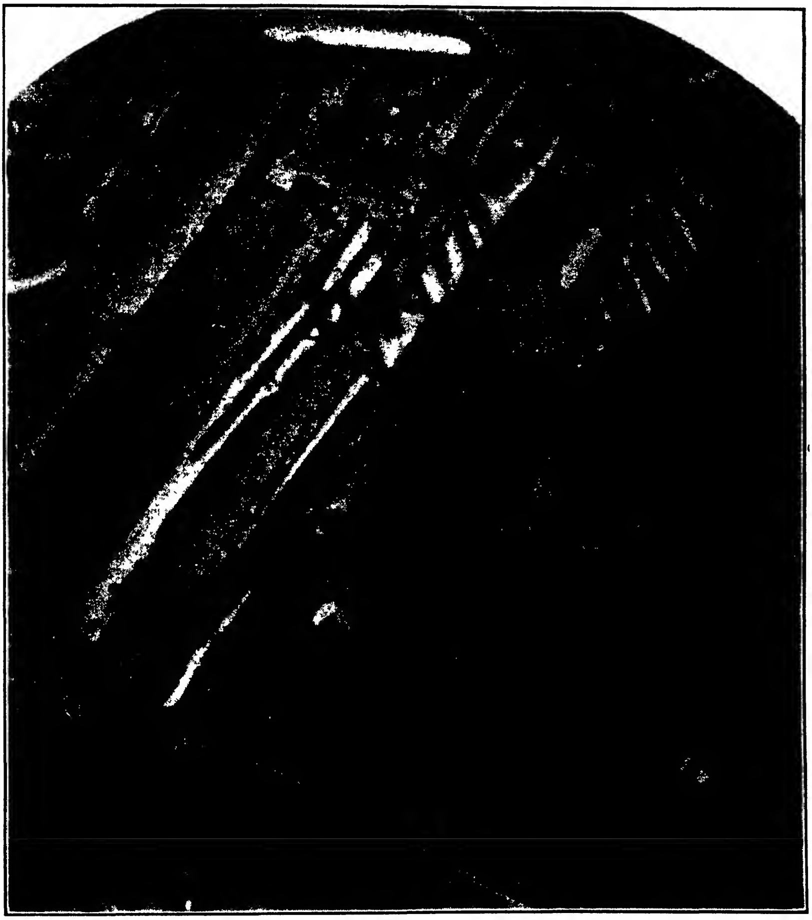

FIG. 6.—CN-7-22 TYPE, ANNEALED; SHOWS SEVERAL CRYSTALS AND SINGLE AND MULTIPLE TWINNING, WHICH IS QUITE CHARACTERISTIC OF AUSTENITIC STEELS OF CHROMIUM-NICKEL SERIES. × 2400.

increasing values with ascending quenching temperatures from 19 to 53 ft.-lb., at which load they bent only and did not break.

It is a great pleasure and privilege to show some illustrations made for this occasion by Francis F. Lucas[6] to whom was recently awarded by the

[6] F. F. Lucas: The Microstructure of Austenite and Martensite. *Trans.* A. S. S. T. (1924) **6**, 669.

American Society for Steel Treating the Henry M. Howe medal in recognition of his notable achievements in metallography. Most of you have seen the results of his splendid work and wonderful technique on other occasions. I doubt, however, whether any of you ever saw some of the remarkable structures here presented. I will not attempt to interpret them but would welcome interpretation from others better able to do so. They will make us appreciate what a vast new field has been opened to

Fig. 7.—Same steel lightly etched with aqua regia, showing peculiar striations vertical to grain boundaries. × 6000.

us for investigation and what results may be attained when the methods of Mr. Lucas become generally available.

It has been my endeavor to present what we may call a cross-section of the field in which we find those steels of maximum general resistance to corrosion, maximum physical properties at actual high temperatures, and maximum resistance to scaling at elevated temperatures. The quarternary alloys offer greater resistance to a wider list of corrosive agents than do the ternary alloys. The latter show good resistance to a more limited

list of chemicals. As to resistance to oxidation at high temperatures, the plain chromium steels are very good and the nickel steels are quite inferior by comparison, but for actual high strength at high temperatures and for resistance to oxidation as well, the quarternary chrome-nickels stand alone, particularly when high silicon is present.

The steels used for these tests were not chosen because they represented the maximum qualities obtainable in any particular; many possible

FIG. 8.—SAME STEEL MORE DEEPLY ETCHED AND SHOWING A PLATEAU EFFECT AT GRAIN BOUNDARY, WHICH SEEMS TO BE SERRATED AND CRYSTALLINE. × 6000.

variations may be made to produce particular results for a particular use. In this subject the art has preceded the science by a long distance and truly remarkable results have been obtained in many industrial applications by the cut-and-try method but our experience is now so broad that some generalizations are possible and some predictions may be made under known conditions of use, but that is another story which we will not consider at this time.

Part II. Austenite

Having described some of the unique physical characteristics of a group of alloys that are of great interest to the chemical, mining, and engineering professions because of those properties, I should like to discuss austenite itself, rather than austenitic steels for the few minutes remaining.

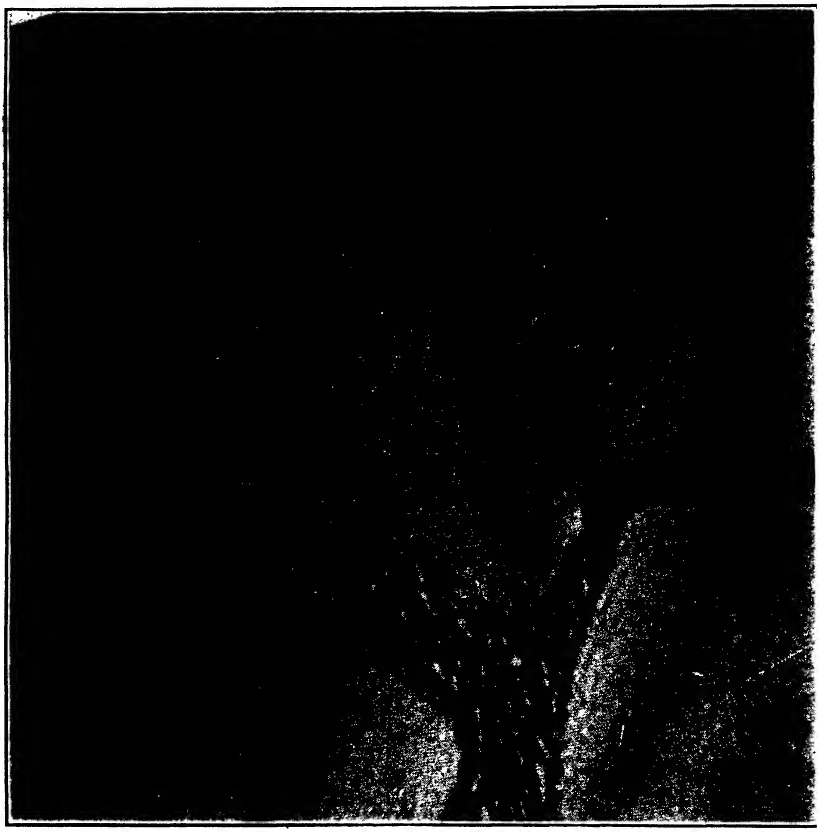

Fig. 9.—Same steel, after quenching at 2400° F. in water, showing grain boundaries; main crystals are but slightly etched and reveal no internal structure. × 2400.

It might be in order first to consider the definition of austenite. The latest authoritative definition is perhaps that of Jeffries and Archer:[7]

> A solid solution of carbon in gamma iron. The iron atoms have face-centered cubic arrangement. The carbon is atomically dispersed. The carbon atoms may be substituted for some of the iron atoms in the face-centered lattice, or more probably occupy positions between the iron atoms. Austenite is relatively soft and ductile.

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[7] Zay Jeffries and R. S. Archer: "The Science of Metals", 443. McGraw-Hill Book Co., New York, 1924.

This definition differs from the older ones in that it adds the evidence of the x-ray. Most textbooks of metallography tell the student how he may prepare steel to show the "austenitic structure." He is told to select a very high carbon sample, preferably high in manganese also, to heat it to 2000° F. and quench drastically in iced brine. After polishing and etching, he sees not austenite but a mixture of austenite and martensite. From this experiment he gains a very strong and lasting impression that austenite is a very rare thing, and so it is in visible form.

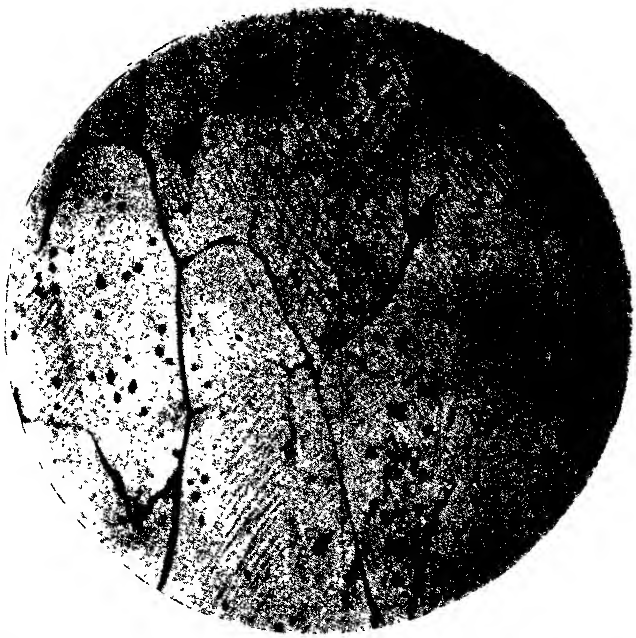


FIG. 10.—STRESSED PORTION OF TENSILE TEST PIECE; SAME TREATMENT AS IN FIG. 9; NOTE ELONGATION OF GRAINS AND SLIP LINES. × 175.

A little later he may see a specimen of fully hardened high-speed steel. He sees distinct polygonal grains interspersed with carbides and is probably told that the grains or crystals are austenite. To be sure, the resemblance to the earlier specimen is not very striking, yet this particular structure is generally referred to as "austenitic." However, if we accept the evidence of the magnetic test, we cannot conclude that this material is free from alpha iron. In fact, it shows a very strong magnetization considering that it is only about 75 per cent. iron to begin with.

In a recent paper by Bain and Jeffries,[8] the authors present two diagrams, based on the best existing evidence, showing the approximate

[8] Edgar C. Bain and Zay Jeffries: Cause of Red Hardness of High-speed Steel. *The Iron Age* (1923) **112**, 805.

constitution of high-speed steel (*a*) as fully hardened and drawn to various temperatures and (*b*) as hardened at various temperatures between 1200° and 2400° F. and not drawn. The relative proportions of austenite, martensite, and carbides are given. It occurred to me to plot on their diagram, the magnetic properties of a typical high-speed steel. The results are shown on Fig. 15. The sudden increase in magnetization (B) with the vanishing austenite component in the upper part and the

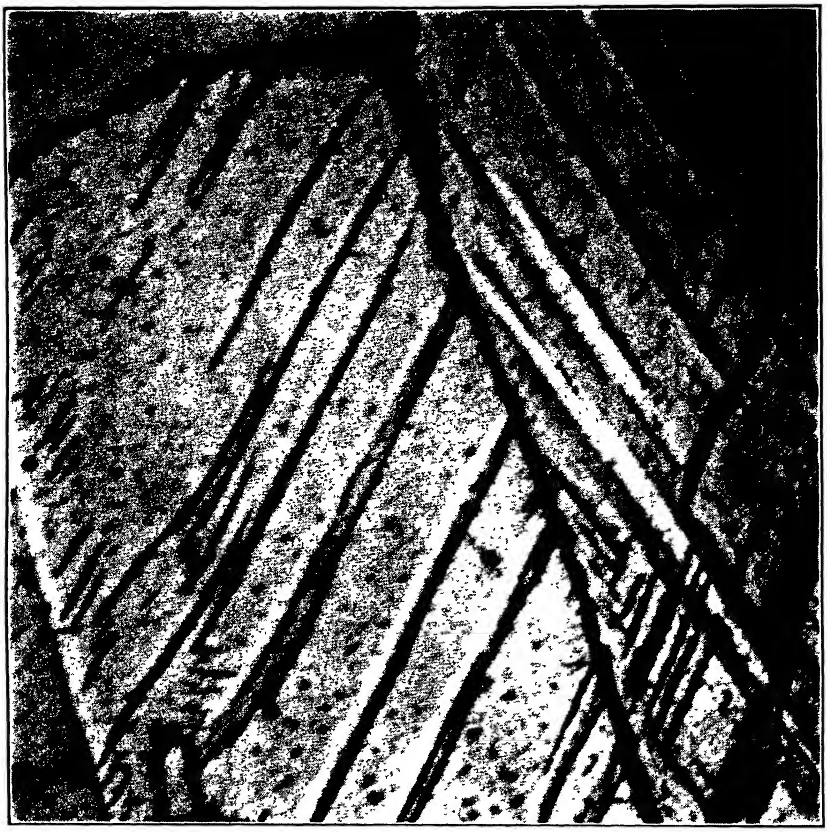


FIG. 11.—SAME AS FIG. 10, SHOWING SLIP LINES AND, IN ONE CASE, TWINNING. × 2400.

equally striking increase in permanence as austenite increases due to ascending hardening temperatures is noteworthy confirmation of Bain and Jeffries' work; this will be referred to again later.

We are all familiar with the iron-carbon diagram and recall the areas marked "austenite;" I fear it is sometimes overlooked that this is an "equilibrium" diagram. Everything looks so nice and orderly in its own compartment that there is danger of trying to apply its lessons to metastable or unstable conditions, such as exist in hardened steel. We

like to think that quenching from a certain temperature produces martensite, and tempering martensite produces troostite, and we have a mental picture of these changes proceeding in a perfectly orderly and circumspect way. Recent work with the x-ray and the high-power microscope shows that these changes are not as orderly and complete as most hardeners or steel treaters believe. Styri, Lucas, and others have shown free ferrite, martensite, and austenite existing in a hypereutectoid steel, with

FIG. 12.—SAME MATERIAL AND TREATMENT; PROLONGED ETCHING REVEALS CURIOUS INTERTWINING FORMS WITHIN A SINGLE CRYSTAL AND CROSSING BOUNDARIES; ETCHING IN RELIEF. × 3230.

possibly a little troostite included for good measure; yet according to most of the instruction we have had that is impossible.

I wish now to present the results of certain observations and experiments, and in what follows I shall proceed on three assumptions:

First, that in all normally hardened medium- or high-carbon steels, and the usual engineering alloy steels, gamma iron, or austenite, is always present with the martensite. I think all of those who have studied the

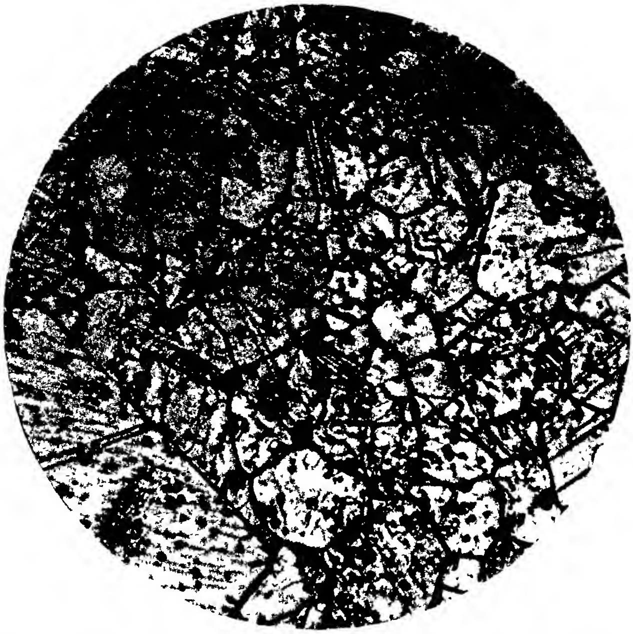


Fig. 13.—A steel intermediate in composition between CN-21-7 and CN-15-15; brine quenched from 2200° F.; note great variety of grain sizes and the frequent twinning. × 175.

Fig. 14.—Same as in Fig. 13; note curious saw-tooth boundaries, having rather a double-line appearance. × 3230.

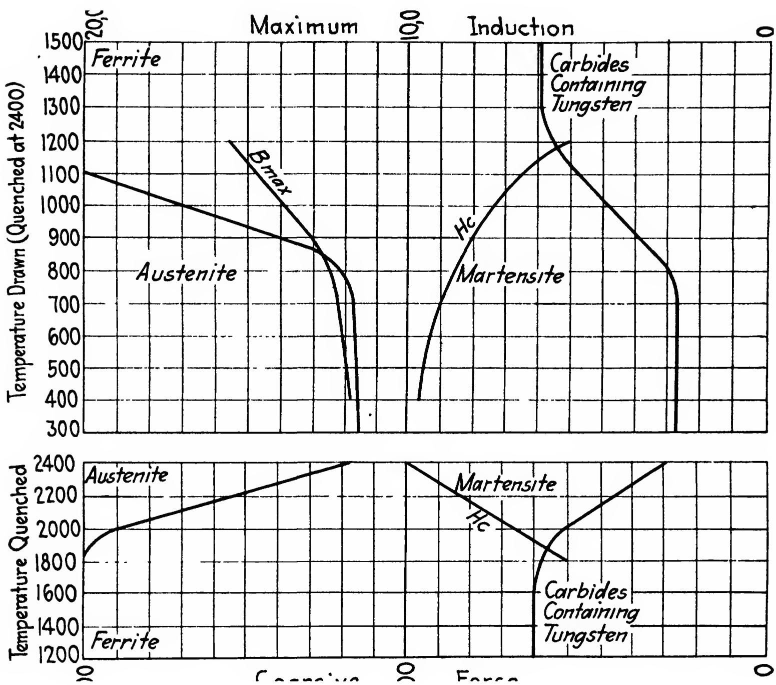


FIG. 15.—BAIN AND JEFFRIES DIAGRAM VS. MAGNETIC PROPERTIES OF HIGH-SPEED STEEL.

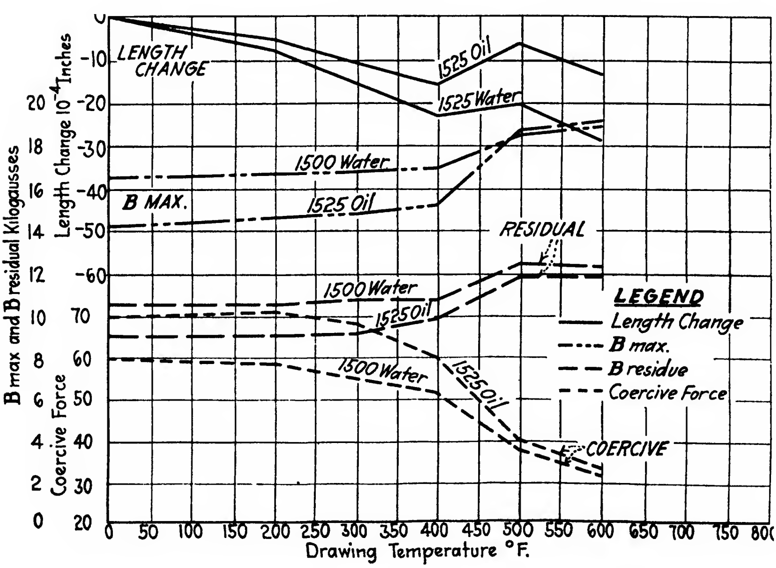


FIG. 16.—EFFECT OF REHEATING IN LENGTH CHANGE AND MAGNETIC PROPERTIES OF QUENCHED CHROME MAGNET STEEL M-31.

volume changes that hardened steels undergo by tempering will readily agree with this assumption. The work of Howard Scott,[9] M. A. Grossmann[10], Heindlhofer and Wright[11] and others strongly point to the reasonableness of this view.

Second, that in a wide variety of alloy steels, notably those capable of hardening readily in oil, there is more austenite retained after the oil quench than after the water quench, in normal hardening. This assumption will not be readily accepted; it is contrary to general opinion and belief. In the metallurgical literature there are many references and allusions to retained austenite but little attempt has been made, so far

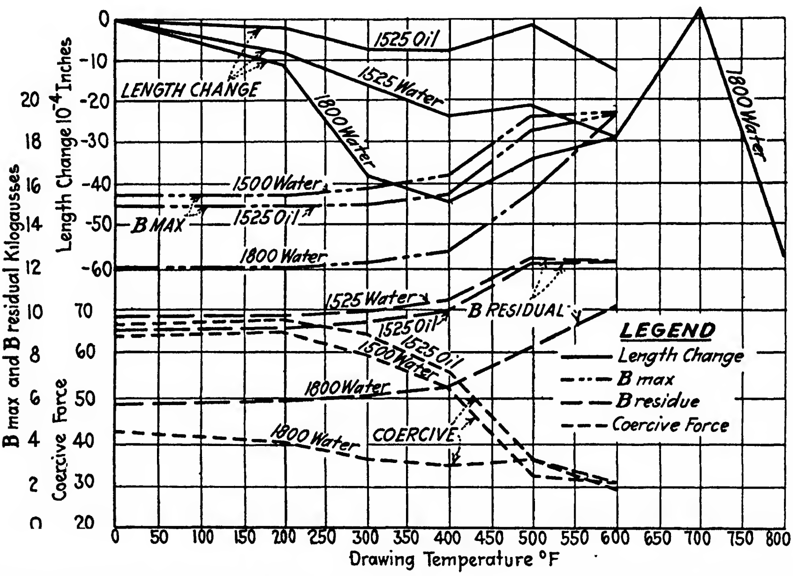


FIG. 17.—EFFECT OF REHEATING ON LENGTH CHANGE AND MAGNETIC PROPERTIES OF QUENCHED CHROME MAGNET STEEL M-62.

as I am aware, to estimate the amount so retained or its effect on hardened steel, nor have the conditions that promote or retard retention of gamma iron been extensively investigated.

Third, that austenite is a cause of increased permanence or retentivity in commercial permanent magnet steels and in many other alloy steels not used for magnets. In the diagram showing the constitution and magnetic properties of high-speed steels, the relation between the increase or decrease in permanence (Hc) as the austenite increases or decreases, is

[9] *Sci. Paper* No. 395, Bur. of Stand. (1920). *Sci. Paper* No. 396, Bur. of Stand. (1920).

[10] Brittle Range in Low-alloy Steels. *The Iron Age* (1924) **114,** 149.

[11] Density and X-ray Spectrum of Hardened Ball Steel. *Trans.* A. S. S. T. (1925) **7,** 34.

very noticeable. Another general illustration that prompts this third assumption is the nature of the newly discovered cobalt magnet steels. These contain from 15 to 35 per cent. of cobalt, added to from 5 to 10 per cent. of the ordinary constituents of permanent magnet steel—

FIG. RESULT OF RAY AMINATION OF OIL AND WATER UENCHED STEE

tungsten, molybdenum, chromium, and manganese. Such steels have strong austenitic characteristics and on overheating for hardening may become almost totally non-magnetic. One test showed only 160 gausses of retained magnetism after quenching from 2000° F. and 375 when quenched from 1900° F. instead of the customary 9000 to 11,000 of good

FIG. 19.—MAGNET STEEL OIL QUENCHED FROM 1525° F. × 2830.

FIG. 20.—MAGNET STEEL WATER QUENCHED FROM 1525° F. × 2830.

magnet steel. A specimen immersed in liquid air had its residual magnetism increased nine times due to transformation of austenite into martensite. It should be recalled that the cobalt steels excel only in high coercive force (Hc) and not in superior maximum or residual magnetism. Table 5 gives a comparison of residual magnetism (Br) and coercive force (Hc) of a few typical tests on cobalt, tungsten, and chrome magnet steels which illustrate this point.

TABLE 5.—*Comparison of Residual Magnetism and Coercive Force in Magnet Steels*

Type	H	Br	Hc
Cobalt No. 1	1500	10,100	237
Cobalt No. 2	750	8,850	155
Cobalt No. 3	750	7,890	193
Tungsten No. 1	300	10,300	71
Tungsten No. 2	300	10,700	66.5
Chromium No. 1 water quenched	300	10,710	60.0
Chromium No. 2 oil quenched	300	8,540	64.5

It will be observed that even when magnetized in a very strong field (H = 1500) the residual magnetism is not higher than the other steels, but that the coercive force is from three to four times as great and, in my opinion, partly because of retained austenite.

In 1914[12] I published the results of certain experiments made under my direction at the Halcomb Steel Co. The principal announcement was the discovery, made a few years earlier, that a large class of alloy steels show greater magnetic hardness when quenched in oil than when quenched in water. The general belief at that time was that the harder one could get a given steel the lower would be its induction and the higher its permanence. This is not the case with such engineering alloys as chrome-nickel, silico-manganese, 3½ per cent. nickel, chrome-silico-manganese, and plain chromium steels. These steels quenched in oil show a much lower Brinell or Shore hardness than if quenched in water and yet are magnetically harder; *i. e.*, more resistant to magnetizing and more permanent after magnetizing.

I made no attempt to explain this but invited an explanation from anyone who could give it. In twelve years I have had none and, as the problem is still awaiting solution, I have attempted to answer my own inquiry. One method of attack was suggested by the work of M. A. Grossmann.[13] In 1921, the writer called attention to the shock brittleness exhibited by many alloys after quenching and drawing to about

[12] J. A. Mathews: The Magnetic Habits of Alloy Steels. *Proc.* A. S. T. M. (1914) **14**.

[13] *Op. cit.*

600° F. This applies to chrome-nickel, chrome-molybdenum, and probably other high tensile engineering steels. In the Izod test, they frequently show less resistance to shock after tempering at 600° than after no tempering at all. Grossmann sought an explanation of this phenomenon by the method of observing the volume changes, or rather length changes, induced in these steels at various drawing temperatures and discovered that the point of greatest shock brittleness seems to coincide with the drawing temperature which produces a quite sudden expansion in the steels, believed to be due to the tempering of austenite. It was decided to apply this method along with magnetic tests to chromium steels known to be magnetically hardest after oil hardening. Two steels were chosen as follows:

	M-31	M-62
Carbon, per cent	0.84	0.91
Silicon, per cent	0.20	0.25
Manganese, per cent	0.47	0.34
Chromium, per cent	2.96	2.16

Test specimens ½ in. round were prepared and hardened at 1500° F. in water and 1525° F. in oil, and the temper was drawn at 100° intervals from 200° to 700° F., holding at temperature ½ hr. Later, the volume changes were repeated hardening both steels in both oil and water from 1525° F.

Figs. 16 and 17 show the results of both the length changes and the corresponding magnetic properties. The shrinkage that first takes place is due to tempering of martensite and the formation and precipitation of carbides. The expansion that begins at 400° F. is due to the austenite-martensite transformation. It will be noticed that the shrinkage in both cases is greatest in the water-hardened steel and the expansion is greatest in the oil-hardened steel, seemingly indicating varying proportions of martensite and austenite present. The magnetic properties closely follow the volume changes and, in several places on the diagrams, the greater change of slope in the oil-hardened steel as compared with the water-hardened strikingly follows the length changes and, in my opinion, strongly supports the view that more austenite is present after oil quenching.

It is known that hardened steel is lighter than annealed steel; in fact, martensite is the lightest, that is, the most voluminous condition of steel. A hardening that produces the lowest specific gravity (greatest volume) may be considered as the most complete martensitization possible for that steel. A hardened steel of greater specific gravity (smaller volume) must indicate retained austenite or that the hardening has gone beyond the martensite stage toward troostite or pearlite. In order to check up on this point, specific-gravity determinations were made not only on the

two chromium steels referred to above, but also on a low chrome-tungsten steel, a chrome-nickel steel, and a 5 per cent. tungsten steel; in every instance the water-hardening produced the lower specific gravity indicating more martensite. The results are as follows:

	Oil Quenched	Water Quenched
M-62 No. 1	7.8548	7.8416
M-62 No. 2	7.7996	7.7861
M-31	7.8371	7.8302
5 per cent. tungsten	8.1292	8.1015
Chrome-nickel	7.8255	7.8177
Chrome-tungsten	7.8755	7.8580

These differences suggest retained austenite in greater amount in the oil-hardened steels but I believe there is some austenite or gamma iron in both cases, as the expansion on tempering above 400° F. would indicate. It should not be assumed, however, that this is a fixed temperature for all steels; *e. g.* the austenite-martensite transformation begins at about 1000° F. in hardened high-speed steel.

In 1922, Tokujiro Matsushita[14] published an article On the Magnetic Hardness of Quenched Steels. The author used the coercive force (Hc) as a criterion of hardness and established various relationships regarding effect of carbon, temperature of quenching, quenching media, etc. He did not attempt to correlate magnetic hardness and physical hardness as measured by the Brinell, Shore, or other methods and most of his work refers to a variable carbon series of steels. In regard to alloy steels, he says: "In alloy steels, which contain a considerable amount of special elements, the velocity of the A_1 transformation is very small; hence if the rate of cooling is large, the transformation austenite to martensite is greatly hindered, so that a part or a greater part of the material remains at the ordinary temperature in the form of austenite. Hence, the magnetic hardness must be smaller in the case of water quenching than in that of oil quenching."

Matsushita also explains the decrease of magnetic hardness (Hc) in carbon steels hardened at too high a temperature as due to untransformed austenite. He illustrates the effect of oil quenching by two examples—one a tungsten steel and the other a chrome-nickel steel. It will be noted that his explanation of the effect of oil-hardening on alloy steels is the generally accepted one and diametrically opposed to my view. However, as has been shown, both types of steels he selected for illustration show a lower specific gravity in water than in oil, indicating more, not less, martensite. Further, if he had determined maximum and residual induction and not merely coercive force, he would have found the steels which, according to his views, contain most austenite and least

[14] *Sci. Reports,* Sendai, Japan. (1922) **11,** 471.

alpha iron, were most highly magnetic, as the writer fully described twelve years ago.

In passing, let me say the coercive force is a very deceptive criterion of hardness; that is, physical hardness. The writer cited an example showing this in the work previously referred to. A certain steel, on oil quenching, showed Brinell 570, Shore 71; and the same steel by water quenching and drawing at 600° F. showed Brinell 567 and Shore 70—certainly a very close agreement in hardness as ordinarily tested—but the coercive forces were respectively 52.5 and 23.0, while the maximum inductions were equally divergent—13,060 and 19,600 respectively. It therefore appears that for a given steel the way a certain hardness is produced has an important bearing upon the accompanying magnetic properties.

Another peculiarity of the magnetic hardness of a given steel is that it appears to increase with increases of size, within certain limits. This again is opposed to the idea that the harder one can make a given steel, and the more drastically one can cool it, the less permeable and more permanent it will become. We first noticed this many years ago but have recently repeated the experiment with a different steel, a different form of testing apparatus, and a different observer. The results fully confirm those published in 1914; the details of the experiment are shown in Table 6.

TABLE 6.—*Effect of Size on Magnetic Properties*

Diameter, Inches	1525° F. Oil			1525° F. Water		
	3/8	1/2	11/16	3/8	1/2	11/16
B max (H = 300)	15,400	15,400	13,600	16,600	16,600	15,500
B res	9,650	9,380	8,780	10,600	10,400	10,300
Hc	60.3	62.2	66.0	55.2	58.1	58.8
Br/Hc	160	151	133	192	179	175

As the size increases, maximum and residual inductions decrease and the coercive force increases for both oil and water hardening; yet the effect of larger size in both cases must be to retard the rate of cooling. The steel used was 0.81 per cent. carbon and 2.91 per cent. chromium, and all three sizes were turned down from a single 3/4-in. bar.

Having arrived at conclusions so contrary to general belief as the results of the experiments just described, it was deemed advisable to get further substantiation and by other methods. I conferred with E. C. Bain and F. F. Lucas and told them of my experiments and the conclusions indicated. Their novelty appealed to them and they volunteered to submit the matter to tests in the fields in which they are

recognized experts. They were furnished samples of the two chromium steels on which our tests were conducted. After magnetic tests had been made, the test pieces were broken in two and one-half of each given to Bain and Lucas.

After examination by the x-ray method Bain reports faint lines corresponding to the pattern for gamma iron in both steels and in both oil and water quenched from 1525° F. (Fig. 18). In the first experiment the lines were too faint to form a basis for a quantitative estimate of the relative amount of gamma iron present in the two conditions of quenching. A further test was made from which he states that it is fairly clear that the oil-hardened specimen shows more gamma iron than the water-hardened specimen. The indications are that the total amount of gamma iron in either case is not very great, perhaps between 6 and 10 per cent.

Lucas examined both steels under high-power magnification; nothing less will reveal anything about the structures of these steels, they are so extremely fine grained. With nitric-acid etching, there was no very great difference in appearance at 3000 magnification, but when boiled in sodium picrate the martensite and carbides were darkened, leaving numerous uncolored areas believed to be austenite. Four or five pictures were taken of each steel as oil or water quenched. It is readily possible to divide these into two groups, depending on the amount of white, uncolored, austenite patches; these are plainly more pronounced in the oil-quenched samples, Figs. 19 and 20, and also more pronounced in the 3 per cent. chromium steel than in the 2 per cent. steel. An attempt was made to transform this austenite into martensite by immersion in liquid air, but while a change is produced by this treatment it manifests itself principally in the way the sodium picrate acts upon the steel and we cannot say that the liquid-air treatment has contributed anything of interest. Most experiments of this kind that have been reported in the past have dealt with richly austenitic steels and it is by no means certain that small amounts of austenite with which we are dealing will be similarly transformed. H. Scott has shown that hardened high-speed steel and a very high carbon and manganese steel, quenched from a high temperature, are materially affected at liquid-air temperature and our experiment with cobalt-magnet steel, previously mentioned, shows the same result.

With this confirmation by independent observers and by additional methods, it seems that the three assumptions made at the outset of this section have been justified by the evidence presented. This new viewpoint as to the nature of the hardening process may prove of considerable interest in interpreting various phenomena met with in our daily work and to me it is a logical explanation of certain magnetic anomalies to which I called attention several years ago, but if I have succeeded in answering my own inquiry, I have at the same time raised another—why

does oil-hardening retain more gamma iron than water-hardening in a considerable variety of steels? It is believed that a deeper investigation of hardening stresses rather than quenching rates may prove the key to the matter, and possibly some future Howe lecturer will give the answer.

It may be that it is an important function of the commoner alloys—chromium, manganese, and nickel, or their mixtures, to promote the retention of gamma iron and that to this fact some of the properties of alloy steels as compared with carbon steels are due. Steel in its heat-treatment does not behave erratically. It follows definite laws associated with considerations of time, mass, speed, pressure, composition, and initial structural condition. I repeat my axiom of heat treatment—constant conditions give constant results. It is because of the practical difficulties of controlling those conditions in production and treatment and because there is still so much to be learned about the fundamental laws and their operation that results are not always what they should be.

In conclusion, let me acknowledge my indebtedness to my associates in several of our laboratories, whose efforts made this lecture possible, and I would particularly mention Mr. P. Peskowitz, who made most of the physical measurements and heat treatments. I am under great obligations to the Bureau of Standards, to Mr. E. C. Bain, of the Union Carbide & Carbon Research Laboratories, Inc., and to Mr. F. F. Lucas, of the Western Electric Research Laboratories, all of whom felt, I am sure, a personal interest in contributing something to this occasion in honor of him whose memory all metallurgists revere—Henry Marion Howe.

Action of Hot Wall: a Factor of Fundamental Influence on the Rapid Corrosion of Water Tubes and Related to the Segregation in Hot Metals*

By Carl Benedicks,† Stockholm, Sweden

It is well known by every one who has had to deal with boiler tubes that these are often seriously affected by a sort of corrosion, occurring as a local pitting, that frequently causes a perforation of the tube in a rather short time. The characteristic appearance of this corrosion is shown in Fig. 1. A very similar corrosion occurs in condenser tubes (Fig. 2).[1] A study of the microstructure or local chemical composition of the metal (iron 70:30 brass) fails to reveal any cause for this pitting. Of course one might possibly assume the starting point to be some oxide particle, causing an electrolytic local action, but this in no way explains the continued corrosion, progressing even when the assumed oxide particle must have disappeared.

By the excellent work done by the Corrosion Research Committee of the Institute of Metals, and communicated, in October, 1923, to the Institution of Engineers and Shipbuilders in Newcastle-on-tyne, stress was laid on the fact that a content of entangled air has a very obnoxious effect. In the following correspondence, Sir George Goodwin stated that "engineers have, for a long time past, regarded air as the big enemy to be fought against in all questions of corrosion"[2] and Kenneth Fraser pointed out that the most vital point is "the avoidance or removal of possibly the chief cause of present day corrosion, *i. e.* entrapped air and gases brought out of solution."[3] In their reply, however, the authors state that they had "never for a moment believed that entangled air was responsible for the beginnings of corrosion, and express the opinion that the gradual liberation of air could not account for localized corrosion."[4] On consulting the many textbooks on corrosion, as that

* Fourth Annual Lecture of the Institute of Metals Division, the American Institute of Mining and Metallurgical Engineers, at the New York Meeting, February, 1925.

† Director of the Metallographic Institute of Stockholm.

[1] Corrosion Research Committee of the Institute of Metals, 7th Report. 1923.

[2] *Loc. cit.*, 62. [3] *Loc. cit.*, 65. [4] *Loc. cit.*, 89.

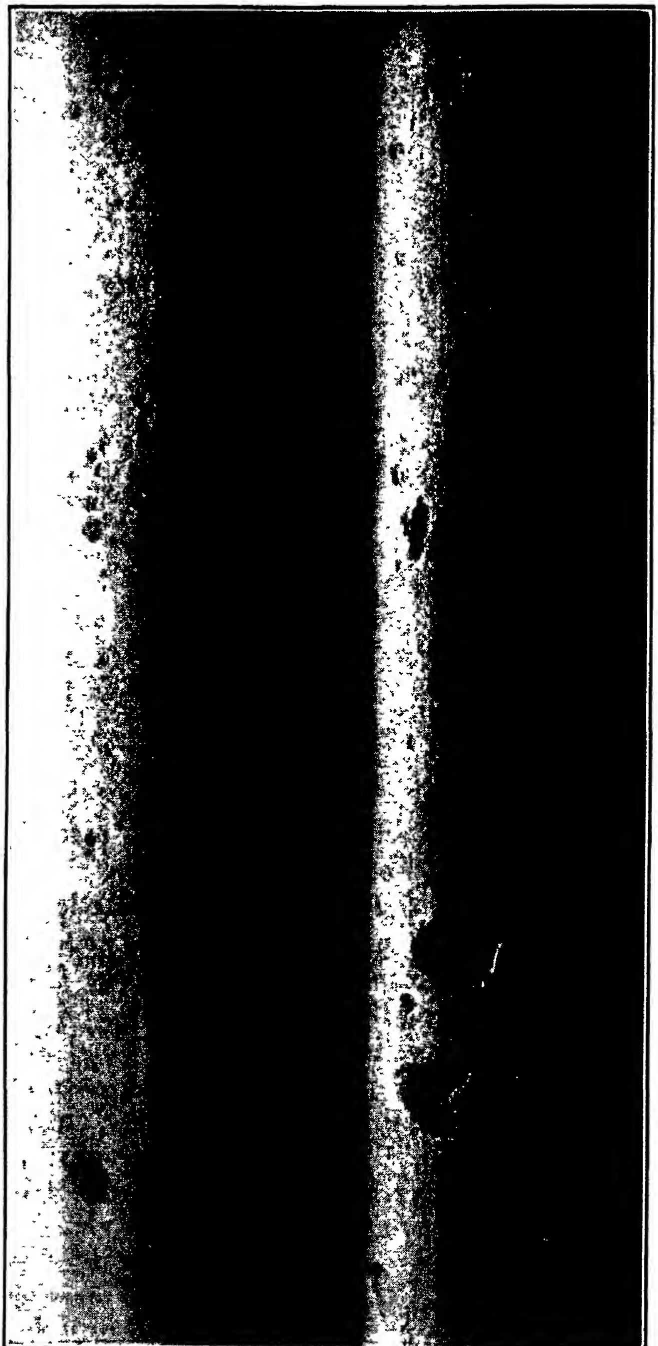


Fig. 1.—Typical pittings on boiler tubes.

published lately by A. A. Pollitt[5] or U. R. Evans,[6] nothing is found that explains this important point.

There is apparently a link missing in the chain of evidence for the deleterious influence of air in water-pipe corrosion. The main object of this lecture is to supply that missing link, by elucidating the problem why air, entangled or dissolved, has so considerable an influence in water-pipe corrosion. We are going to find that the key is given by an effect that has hitherto been overlooked, not strictly belonging to chemistry or to metallurgy, or to engineering. It is, on the contrary, a purely physical effect, which we are going to designate as the action of the hot wall.

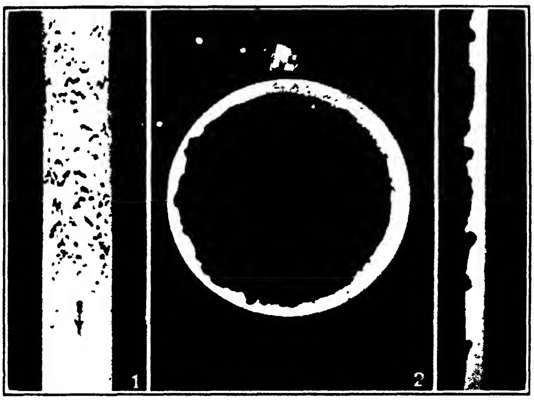


FIG. 2.—PITTINGS ON CONDENSER TUBES, ACCORDING TO BENGOUGH, MAY AND PIRRET.

Having elucidated this factor in thermal corrosion, it will be easy for us to proceed to the invention of a practical method for preventing its action. Then this effect will be regarded as being the special case of a more general effect which is not altogether unknown to physical chemistry; *viz.* the so-called Ludwig-Soret's phenomenon, occurring in salt solutions when subjected to temperature differences.

Finally, we shall see that some phenomena of importance to metallurgy, and to metallography—a kind of segregation in molten alloys—will be eluciated by this phenomenon, and that it has probably a notable influence, though neglected so far in the domain of solid solutions.

ACTION OF THE HOT WALL AS THE CHIEF CAUSE OF CORROSION

In his Carnegie scholarship work of 1908, the author availed himself of the determination of the cooling power of liquids as being of importance for steel quenching. In the most direct method employed, an electrically heated platinum wire was surrounded by a stream of the liquid

[5] A. A. Pollitt: "The Causes and Prevention of Corrosion." London, 1923.
[6] U. R. Evans: "The Corrosion of Metals." London, 1924.

to be tested. It was found, however, that this method was impracticable for ordinary water. The platinum wire, even at a comparatively low electrical current strength, was locally overheated, which caused the wire to melt off. This rather unexpected behavior of the wire was found to have the following origin: from the streaming water containing dissolved (no entangled) air, some gas was deposited on a given spot of the wire and the air bubble thus formed prevented the liquid from cooling; hence the local overheating. The adhesion of the air to the hot wire, presumably to some spot of slightly higher temperature, was found to be so great that no practicable increase of the water speed prevented it. The only prevention was to render the water air-free, which was effected by prolonged boiling and subsequent cooling (say under liquid paraffine).

Later, having to deal with some badly corroded boiler tubes, the author found that the local pitting must be closely connected with the local overheating experienced in the case of the platinum wire. As a matter of fact, and as was borne out by some simple experiments, the action met with on platinum must be a general one.

As is well known, even in homogeneous moist air a new phase (liquid water) appears on every point where the temperature is below a definite value (the dew point). This implies that the partial pressure of the water is determined by the lowest temperature occurring. This is often designated as "the action of the cold wall." On the other hand, in a liquid containing air, or another gas, in solution, a new phase (gas) will appear on every point where the temperature is above a definite value (depending on the concentration and solubility of the gas). This implies that the partial pressure of the dissolved gas is determined by the highest temperature occurring. In order to have the analogy borne out as clearly as possible, we will designate this as "the action of the hot wall."

We may comprise both cases under the same rule: Given a homogeneous solution of any aggregation state, phase A: If then the solubility of the solute decreases with decreasing temperature, a new phase B, which is richer in the solute, will appear at a point of (sufficiently) low temperature (action of the cold wall). If the solubility decreases with increasing temperature, the new phase B will appear at a point of (sufficiently, high temperature (action of the hot wall).

As the case in which solubility decreases with decreasing temperature (or increases with increasing temperature) is much more frequent than the case of a solubility decreasing with increasing temperature, we easily realize that the action of the cold wall has received a certain amount of attention, which has not been the case with the action of the hot wall.

Both follow so directly from the well-known laws of heterogeneous equilibrium that no actual deduction is necessary. Likewise, no demonstration is needed to illustrate the action of the cold wall; at least during

winter time every wearer of spectacles experiences its influence more frequently than he likes. On the contrary, some demonstration of the action of the hot wall is desirable, as this is much less familiar to us.

As a first demonstration of the action of the hot wall, the following experiment may be described. A thin platinum strip *ABC*, Fig. 3, the width of which is variable, is pressed in between two electrodes fixed in a rubber-tightened wooden cover *D* of a horizontal cuvette *E*, through which a stream of aërated water passes. When a weak current is passed through the platinum strip, the narrow part *A* is sensibly heated and a considerable number of air bubbles are precipitated on it. If the current intensity is increased, air bubbles will also be deposited on *B*; at a still higher intensity of current, some bubbles will also appear on *C*. The aspect of the strip in the three cases is shown in Fig. 4, (*a*), (*b*), (*c*); the air bubbles are shown to have formed in preference on the hottest parts in contact with the liquid.

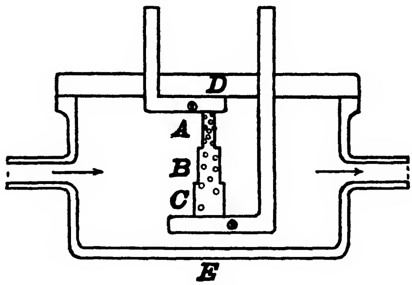
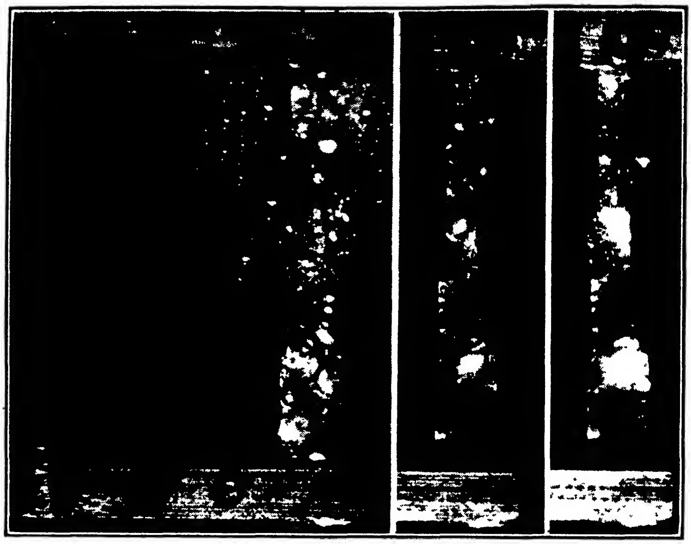


FIG. 3.—ARRANGEMENT OF DEMONSTRATION APPARATUS.

In order further to demonstrate that the points where air is precipitated are apt to become superheated, a considerable number of experiments were carried out, thin strips of platinum (0.02 mm.) as well as of silver and tin being used; but these proved to be failures. From these negative experiments, however, a result important for the later work was obtained: it was found that a sufficiently thin, electrically heated metal strip, even when immersed in aërated water, is but little affected by local superheating due to adhering air, for the reason that there is but little probability that an air bubble will be formed simultaneously on both sides of the strip at the same point; as a matter of fact, the undisturbed cooling from one side generally prevents any considerable superheating.

However, this stability of thin immersed strips must not be overrated. In one of the experiments a thin strip of nichrome tape (1.0 by 0.10 mm.) was electrically heated in aërated water, with the long axis horizontal and the tape plane vertical. In some cases, on passage of the current, air bubbles were formed at the lower edge of the tape, projecting on both sides; the result is shown in Fig. 5. At two points of the lower edge, a superheating has taken place, with a partial melting of the metal; a "pitting" of the tape may be said to be caused in a purely thermic way.

At all events, to enable us to demonstrate this local superheating in a more convenient way—as follows from the above experiments—the



c b a

FIG. 4.—SUCCESSIVE APPEARANCES OF AIR BUBBLES ON PLATINUM STRIP SHOWN IN FIG. 3.

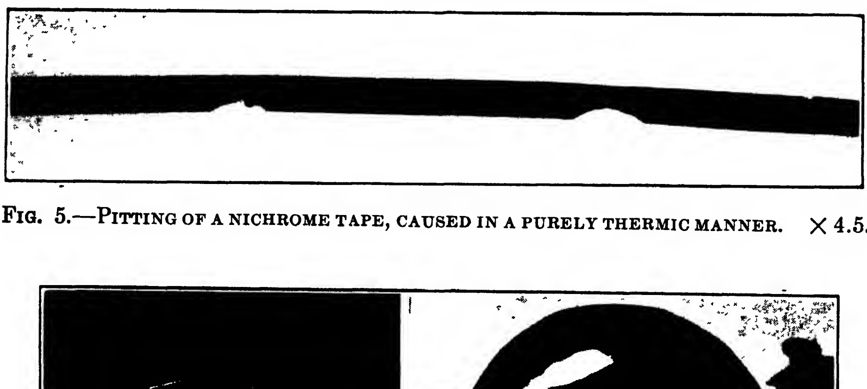


FIG. 5.—PITTING OF A NICHROME TAPE, CAUSED IN A PURELY THERMIC MANNER. × 4.5.

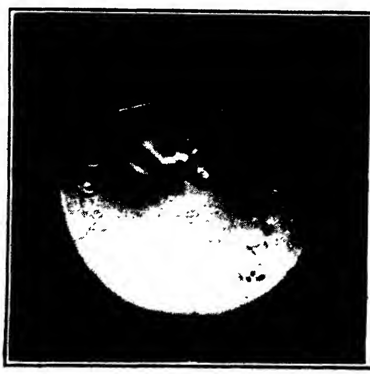


FIG. 6.—THERMICALLY PITTED PLATE OF FUSIBLE ALLOY, IN REFLECTED LIGHT. × 0.7.

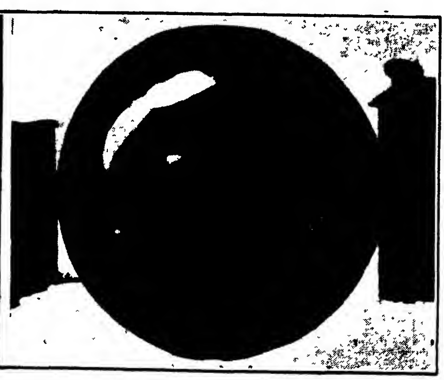


FIG. 7.—SAME AS FIG. 6, IN TRANSMITTED LIGHT. × 0.7.

metal plate must be cooled only from one surface, as is the case with boiler or condenser tubes. Accordingly, the final demonstration experiment was carried out as follows: A plate 0.3 mm. thick was rolled out from the low-melting Newton's alloy (melting point 94.5°; Bi. 8, Pb. 5, Sn. 3 parts by weight). A round disk (60 mm.) of this alloy was heated from below by steam, which could be slightly overheated, while the upper side was cooled by a water stream; the resulting appearance of the disk, by reflected light, is shown in Fig. 6, magnification 0.7, and by transmitted light in Fig. 7. On account of the low melting point of the alloy, local melting and perforation have taken place at some points, where adherent air has diminished the intensity of the water cooling of

FIG. 8.—ASPECT OF A SINGLE THERMIC PITTING. $\times$ 10.

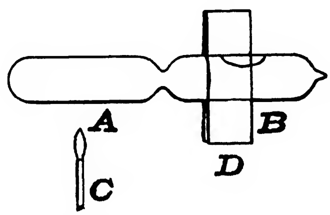


FIG. 9.—APPARATUS FOR DEMONSTRATION OF HOT-WALL ACTION.

the upper surface. The characteristic aspect of such a purely thermic "pitting" of the heated and cooled metal may also be seen in Fig. 8.

The next step in the demonstration would naturally be that of evidencing that the local heatings considered, while not intense enough for causing the metal to melt, in the case of a base metal such as iron or brass, will cause a much accelerated chemical attack by the water, or more strictly speaking by the water vapor, or oxygen, contained in the adherent air. Such a demonstration, however, cannot be considered as necessary, as it is well known to every chemist how rapidly chemical activity increases with temperature. To give a single chemical example: the speed of saponification is known to become doubled on a temperature increase of only 10° C.

We will refer instead to another purely physical demonstration experiment concerning the action of the hot wall. In Fig. 9, *AB* is a glass tube with a strangulation in the middle; when nearly filled with water the tube was sealed. The compartment *A* may be quite filled with water while *B* contains an air bubble as indicated. If *A* is heated by a microflame *C* placed below it while *B* is air-cooled by a strip of copper plate *D*, in a short time the air bubble in *B* will "distill" over to the hot wall and be found in *A*.

Conclusion

In water-tube corrosion, the air content of the water has already been considered as dangerous (perhaps largely on account of its oxygen content), but on the other hand, no reason has been found for this air or oxygen content to cause any local corrosion or pitting of the metal—the most dangerous form of attack.

It has been established that a purely physical—rather paradoxical—effect must influence the problem, *viz.*, the "action of the hot wall," implying that from air-containing water a gas phase is precipitated on the hottest points of the wall—in a way similar to the precipitation from moist air of a liquid phase on the coldest bodies in contact with it.

This local precipitation of air will, on definite points, necessarily prevent the water from exerting its cooling power on these points, and the result will be a considerable temperature increase there. As has been demonstrated, this local superheating, under given circumstances, can give rise to a local, purely thermal pitting of the metal wall; further, if chemical action comes into play, the local superheatings *a fortiori* will cause local corrosion of the metal. This action must be self-accelerating; the deeper the pittings already formed, the greater the local variation in temperature and in air precipitation, with resulting further increase in temperature difference and in corrosion. This being so, we also obtain the explanation of the fact that two metals so different in character as iron and brass seem to behave in a very similar way.

The important question is how to counteract this obnoxious corrosion.

1. It is evident that the surface of the metal must be as even or smooth as possible (the tube thickness as regular and the metal itself as homogeneous as possible). Any metallic projections from the surface are liable to act as centers for the formation of the gas phase. This conclusion, however, is not new, as from nearly every point of view in corrosion the smoothness of the surface is desirable. Unfortunately, from the standpoint of the practical engineer, only little can be done in this direction.

2. It is obvious that the formation of an even sea-scale layer on the metal surface—at least if not too thick—must protect the tube in lessening the effect of any temperature differences that may exist in the metallic surface. This likewise conforms to full earlier experience, but little can be done, as it seems, in this direction.

3. If the tube surface is originally very smooth a high speed of the water is likely to be in opposition to the air precipitation, though probably in no way excluding it; on the other hand, if the surface is roughened, a very high speed will scarcely have any beneficial influence.

4. The only radical means to avoid corrosion will be to remove the possibility of air precipitation in using a water devoid of air. This, likewise, is no novel conclusion: on the contrary practical means of removing the air content of water is an old desideratum. Here, however, the chemical method is out of the question, as the nitrogen that is then left unremoved will exert the same influence of local superheating. The physical method used hitherto, involving the combination of heating and vacuum, signifies a considerable complication. It is therefore very fortunate that the elucidation gained as to the main cause of this corrosion will at the same time offer the rational remedy, "elements beaten with their own arms," or "*elementa suis armis devicta,*" being a sound principle. As a matter of fact, the action of the hot wall may be taken advantage of in order to remove the air, or other gases, at places where it causes no harm.

The Remedy: Rational Air Removal

The most effective way of removing moisture from air probably is to let the air pass over a body of very low temperature (as that of liquid air); the action of the cold wall then causes a removal of every trace of water. *Per analogiam,* we may conclude that a very effective way of removing air from liquid water must be to let the water pass over a body of very high temperature; the action of the hot wall will then probably cause a very energetic air removal.

First Experimental Apparatus

To test the truth of this conclusion, the apparatus shown in Fig. 10 was built up. From a large Mariotte bottle A water flows at a constant speed, which is read on the checking tube B, through two similar glass vessels I and II. Through rubber stops in their lower openings, two thick insulated copper wires are inserted; between them are fixed the heating spirals C_1, and C_2 each consisting of a (150 by 1.0 by 0.1 mm.) nichrome tape, mounted as a spiral and having a resistance of 2.69 ohms each, at +18° C. The upper parts of I and II are graduated and contain stop-cocks; the temperature of the water after passing the heaters is read on the Hg-thermometers D_1 and D_2.

To avoid any electrolysis of the water, alternating current of 50 cycles per sec. at 300 volts is used. After passing a measuring transformer E, the current strength is read on the precision ammeter F while on the wattmeter G is read the energy consumed either by I or by $I + II$. Photographs of the apparatus proper and of the total experimental arrangement are shown in Figs. 11 and 12.

Each experiment was carried out in the following order: A constant water speed being secured and the vessels *I* and *II* being filled with water, the current was switched on at a given moment (after a preliminary adjustment of suitable resistances). At given time intervals, the volume of the air liberated in *I* and *II* was read (in the first series), and readings

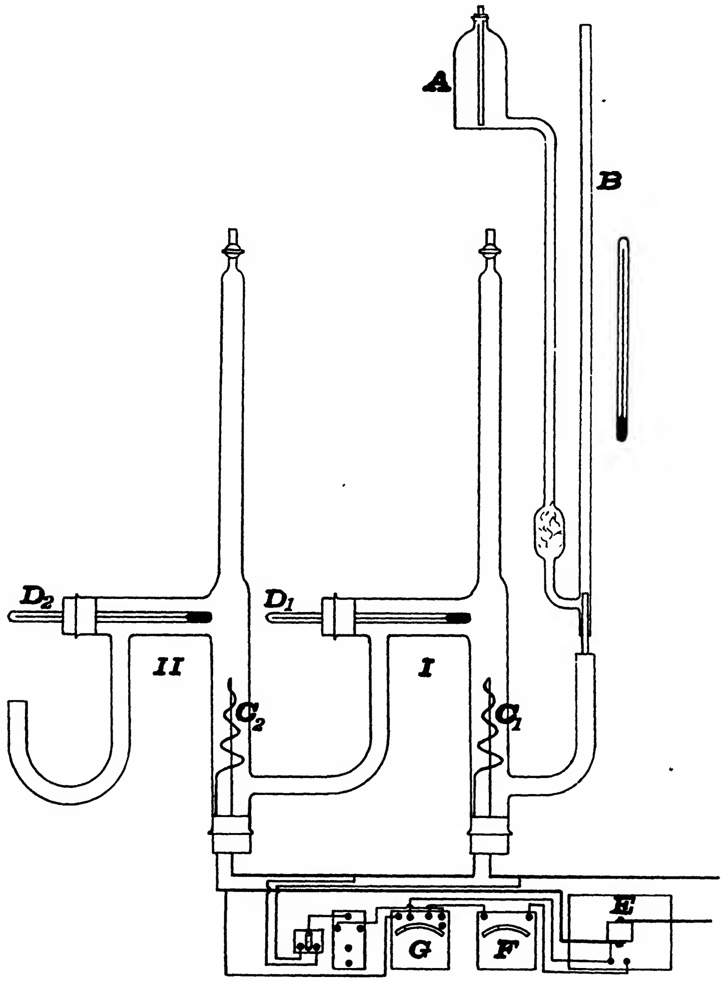


Fig. 10.—Apparatus used for air removal.

taken of the different variables, as given in the following tables. After a definite time the current was broken and the vessels *I* and *II* allowed to cool. The volumes of the air contained in *I* and in *II* were then accurately ascertained after transfer into a gas burette containing salt solution. The first series executed is given in full in Table 1. The main figures of the series executed are compiled in Table 2.

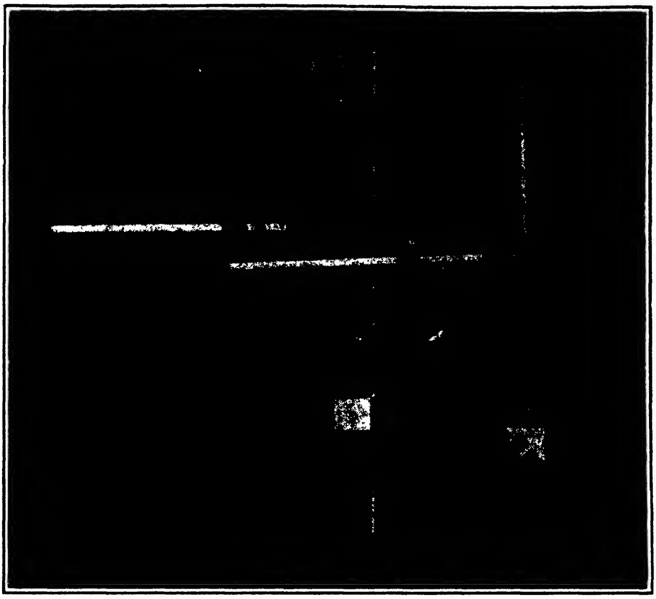


FIG. 11.—AIR-REMOVAL APPARATUS AS SET UP.

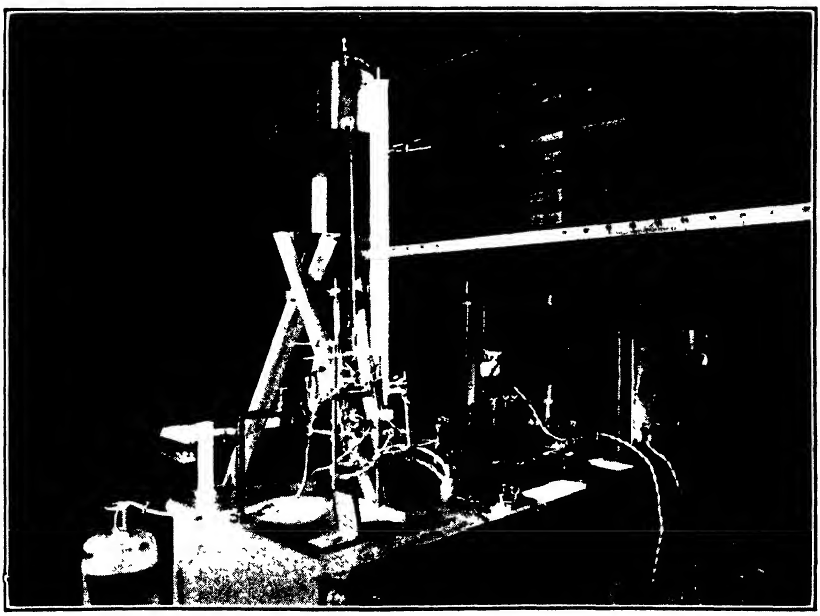


FIG. 12.—FIRST EXPERIMENTAL APPARATUS AS SET UP.

TABLE 1

Date and Series No.	Time, Min.	Water Speed Reading		Current Intensity in ¼ Amp.	Energy		Temperature			Gas Volume (760 Mm., 20° C.)				
		Min.	Per Min.		I in 30 Watt	$I+II$ in 30 Watt	T_0 °C.	T_1 °C.	T_2 °C.	I Cm.³	II Cm.³	I Cm.³/l	II Cm.³/l	Total $I+II$ Cm.³/l
Oct. 2, 1924 1	0	128					19.5							
	3	129		39.5	4.2	10 2		30.0	48.0					
	5	130		29.2	4.0	10.0		30.0	47.5		1.3			
	12	132		38.8	4.0	10.05		30.0	47.5	1.0	3.1			
	20	133		38.7	4.0	10 0		29.8	47.6	1.6	5.0			
	25	133		38.5	3.9	10 0		29.8	47.4	1.9	6.0			
	25	130	150	38.9	4.0	10.05	19.5	29.9	47.6	2.2[a]	6.5[a]	0.6	1.7	2.3

[a] Final determination.

Stationary State

In Fig. 13 are given graphically as small circles the successive gas volume observations of the first two series. The finally determined values are given as dots. There is a strict proportionality between liberated air and time used, showing that the conditions are stationary. (At a higher current the volumes read off successively were less regular on account of the increasing temperature in the upper parts of *I* and *II* influencing the volume readings).

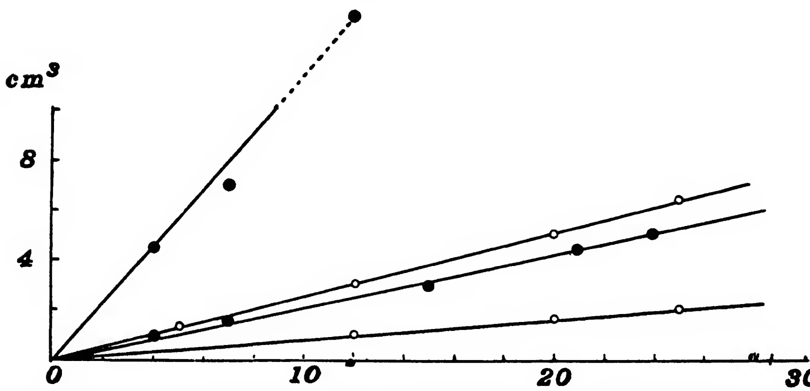


FIG. 13.—CONNECTION BETWEEN LIBERATED AIR AND DURATION OF EXPERIMENT.

Reproducibility

As will be seen from series 5′ and 5″, Table 2, having sensibly the same water speed and energy consumption, the reproducibility is fairly good, at least in view of the fact that the volume observed in 5′, according to the record made, was too small because some air containing steam was lost in this case. Anyhow, the volume readings obtained with this apparatus are slightly too low as the off-flowing water contained a certain amount of entangled air.

Amount of Air Separated

As to the main point: the air quantity separated, as given in column 18, Table 2, already in series 5″, amounted to about 18 cm.[3] per liter. The distilled water gave a figure slightly lower, or 16.2 cm.[3] (series 9). Now, the air content of pure water, saturated with air, according to determinations by L. W. Winkler[7] at +20° C. is 18.7 cm.[3] air (at 760 mm. 0°), or at +20° C. is 20.1 cm.[3] (of 760 mm. and 20°).

To ascertain how much air is actually contained, a special determination was carried out. In this 50 cm.[3] was boiled in a vacuum; the quantity of air given off was determined over mercury by pressure meas-

[7] *Landolt-Börnstein-Both-Scheel: Phys-chem. Tabellen,* 5 Aufl. Berlin, 1923, S. 766.

TABLE 2

Series No.	Date 1924	Time, Min.	Water Speed Cm.³/Min.	Volume of Water, Liters	Intensity of Current, Amperes	Energy: I Watts	Energy: II Watts	Energy: Total Watts	$10^3 \times \frac{\text{Total Watt-sec.}}{\text{Liters}}$	Temperature: T_0 °C.	Temperature: T_1 °C.	Temperature: T_2 °C.	Gas Volume (760 Mm., 20° C.): I Cm.³	II Cm.³	I Cm.³/l	II Cm.³/l	Total Cm.³/l
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	2/10	25	150	3,750	9.7	120	181.5	301.5	120.5	19 5	29.9	47.6	2.2	6.5	0.6	1.7	2.3
2[a]	2/10	25	150	3,750	12.1	183	291	474	189.5	20 0	35.8	64.2	5.2	26.5	1.6	7.1	8.7
3[b]	3/10	25	150	3,750	7.4	150	153	303	121.1	19 0	31.3	44.3	4.2	5.2	1.1	1.4	2.5
4	3/10	25	150	3,750	9.8	267	261	528	211 0	18 6	42 1	66.4	10.6	20.9	2.8	5.6	8.4
5′	3/10	8.5	150	1,275	12.3	417	408	825	330 5	18.6	54 8	89.8	7.8	14.1	6.1	11.1	17.2
5″	3/10	7.0	150	1,050	12.2	408	417	825	330.0	18.6	55 2	90.5	6.9	12.1	6.6	11.5	18.1
6	4/10	20	140	2,800	9.8	267	261	528	226.0	18.0	43 6	70.4	6.2	17.2	2.2	6.1	8.3
7	4/10	6	140	0,840	11 9	393	390	783	345.5	18.5	57.5	94.0	5.7	9.5	6.8	11.3	17.1
8[c]	7/10	20.2	153	3,090	9.8	267	264	531	208.5	19 0	42.9	66.6	5.5	15.9	1.7	4.9	6.6
9	7/10	7.75	157	1,215	12.2	402	411	813	311.5	19 0	56.1	91.0	6.6	13.1	5.4	10.8	16.2
10	7/10	6.7	157	1,050	12.2	411	411	822	315.0	19 0	55.3	87.8	4.8	11.2	4.6	10.7	15.3

[a] Series 1 and 2 being considered as of a preliminary character, the spirals were not of the size mentioned, the resistance at room temperature for *I* being 1.25 ohms, for *II* 1.92 ohms.

[b] Series 3–7 refer to ordinary water. It is not possible to give the exact composition of this water, as no special analysis was made and the composition, according to a communication by Dr. K. Sondén, is rather variable. An idea of its character, however, may be obtained from the fact that the water of the main supply, the Lake Bornsjön, according to the latest analysis published, gave as evaporation residue 0.114 gram per liter, after ignition 0.079 gram per liter.

[c] Series 8–10 refer to distilled water.

uring. By this direct method an air content at +19° C., amounting to 16.5 cm.³ (760 mm., 19°) was found with an uncertainty of about ±1.0 cm.³; to this gas content some combined carbon dioxide, not appearing in the analysis, might have to be added.

From this we may conclude that by far the greatest part of the air content of the water has been separated, using the new separating apparatus. The fact that somewhat more air was obtained from the ordinary water than from the distilled water is probably due to the latter not being quite saturated.

Energy Consumption

With respect to the energy consumption involved in the separation of air from the water, it is easy, from the figures given in Table 2, to compare the energy consumed with the energy taken up in the heating of the water. It is found that, on the average, 93.8 per cent. of the energy used is recovered in the heating of the water. Thus, the loss, due to radiation (final temperature of the water is 94° maximum) does not exceed 10 per cent.; it could easily be diminished by insulation.

Of course the air separation in itself demands a certain amount of energy. As is well known, the work done against atmospheric pressure in developing 1 mol of a gas (24,000 cm.³ at 20°) is given by the formula $W = 1.99 \times T$ cal. $= 581$ cal. for $T = 273 + 20°$. The work done in separating 20 cm.³ per liter accordingly will be only 0.5 cal. per liter; *i. e.*, corresponding to the heating of 1 liter of water from 0° to 0.0005°, or a quantity entirely negligible.

Second Experimental Apparatus

With the apparatus already described a certain air loss could not be avoided, because the water flowing off contained some visible entangled air and possibly also some dissolved air. On this account, an apparatus of improved construction was made; see Fig. 14. It contains three air separators *I*, *II*, and *III*, placed in series, each containing two heating bodies (same nichrome tape as before, but of varying length).

The intention with this was that the first air separator *I* should at once communicate a considerable amount of energy to the water so that the main air quantity would be separated in *I*, while the smaller part remaining would be separated in *II*, and *III* would act merely as a check of the effective result, giving only a very small air quantity, and preventing any entangled air from escaping. To utilize this scheme, it was necessary to be able to vary the relative amount of current sent through *I*, *II* and *III*, respectively. Hence, in series 11 and 12 (Table 3) shunt circuits were arranged according to the scheme given in Fig. 15*a*, permitting a much stronger current through *I*1 and *I*2 than through the others. It was found better to use the connection Fig. 15*b*, where the

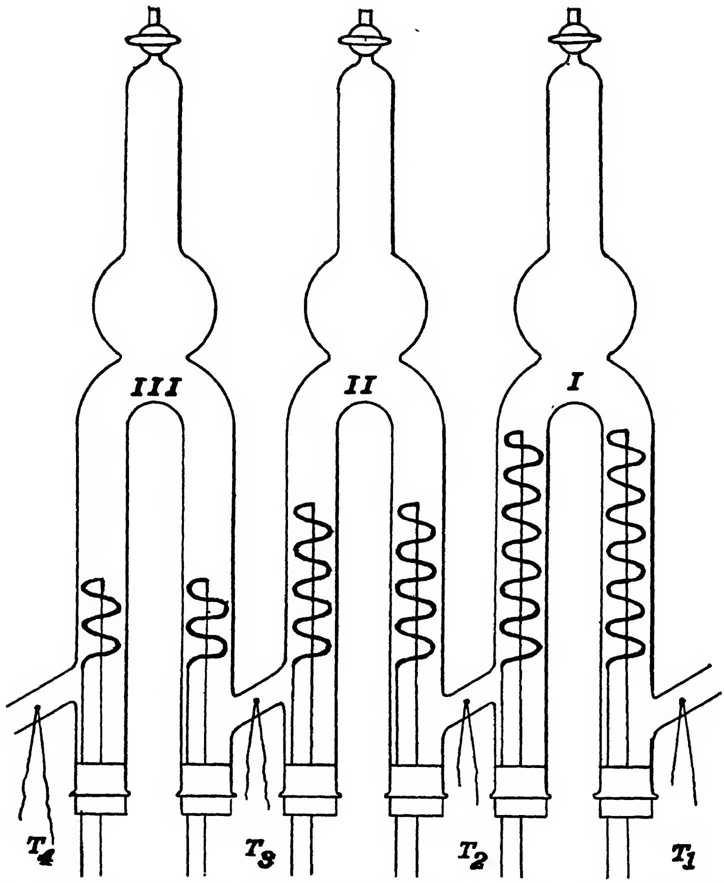


FIG. 14.—SECOND EXPERIMENTAL APPARATUS USED FOR AIR REMOVAL.

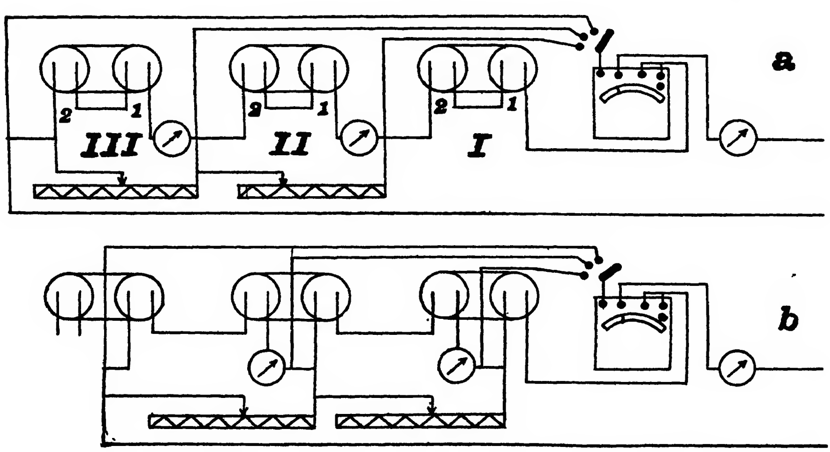


FIG. 15.—WIRING PLANS FOR AIR-REMOVAL APPARATUS.

strong current was passed only through $I1$, as otherwise a considerable boiling took place in $I2$. The lengths of tape and the resistance at room temperature of the heating spirals were as follows:

No.	Length of Tape, Mm.	Resistance, Ohms
$I1$	200	2.65
$I2$	200	2.64
$II1$	100	1.58
$II2$	100	1.41
$III1$	50	0.71
$III2$	50	0.70

With the second apparatus, the temperature was measured by using four iron-constantan thermocouples T_1, T_2, T_3, T_4 inserted in the water pipes, as shown in Fig. 14; their indications were registered with the aid of a Double Thread Recorder. The temperature values given (Table 3) are mean values as read on the registrations. Fig. 16 shows the air

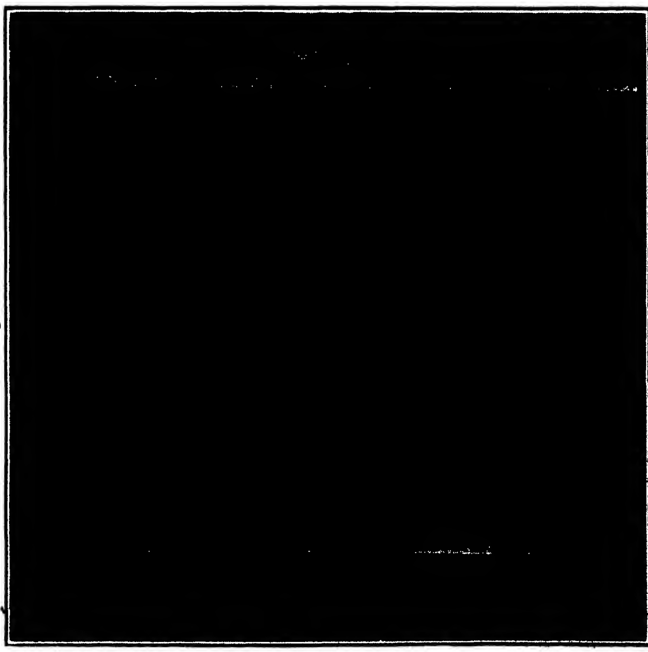


Fig. 16.—Second air-removal apparatus as set up.

separators of the second apparatus as set up; separator I is to the right (large air volume). Fig. 17 shows the complete apparatus as set up.

The results of the four series of tests made are given in Table 3. Only ordinary water was used in this case. As shown by the last column, the quantity of air in series 11 and 12 amounts to 16.4 and 17.0 cm.^{3} per liter, respectively; or sensibly the same amounts as were obtained with the

TABLE 3

Series No.	Date 1924	Time, Min.	Water Speed $\frac{Cm.^3}{Min.}$	Volume of Water, Liters	Intensity of Current I Amp.	II Amp.	III Amp.	Energy I Watts	II Watts	III Watts	Total Watts	$10^3 \times \frac{\text{Total Watt-sec.}}{\text{Liter}}$	Temperature T_0 °C.	T_1 °C.	T_2 °C.	T_3 °C.	Gas Volume (760 Mm., 20° C.) I Cm.³	II Cm.³	III Cm.³	I $\frac{Cm.^3}{l}$	II $\frac{Cm.^3}{l}$	III $\frac{Cm.^3}{l}$	Total $\frac{Cm.^3}{l}$
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
11	17/10	23	162	3.724	12.1	6.9	5.9	738	137	50	425	342.5	19	73	94	96	39.9	16.0	5.1	10.7	4.3	1.4	16.4
12	17/10	24	162	3.888	12.9	7.5	6.8	780	157	76	1013	375.5	18	83	91	93	46.3	11.1	8.6	11.9	2.9	2.2	17.0
13	18/10	22	163	3.585	13.9	9.4	6.6	519	313	95	927	341.5	18	86	95	98	36.6	28.4	3.1	10.2	7.9	0.9	19.0
14	20/10	20	157	3.138	16.1	7.3	5.1	705	184	58	947	361 0	20	91	98	96	45.2	15.3	2.0	14.4	4.9	0.6	19.9

first apparatus. In series 13 and 14, using the better shunting indicated in Fig. 15*b* the total air volume obtained, 19.0 and 19.9 $cm.^3$ (760 mm., 20°), coincides with the Landolt-Börnstein figure already referred to—20.1 $cm.^3$ (760 mm., 20°). Thus, the result is to be considered as a very

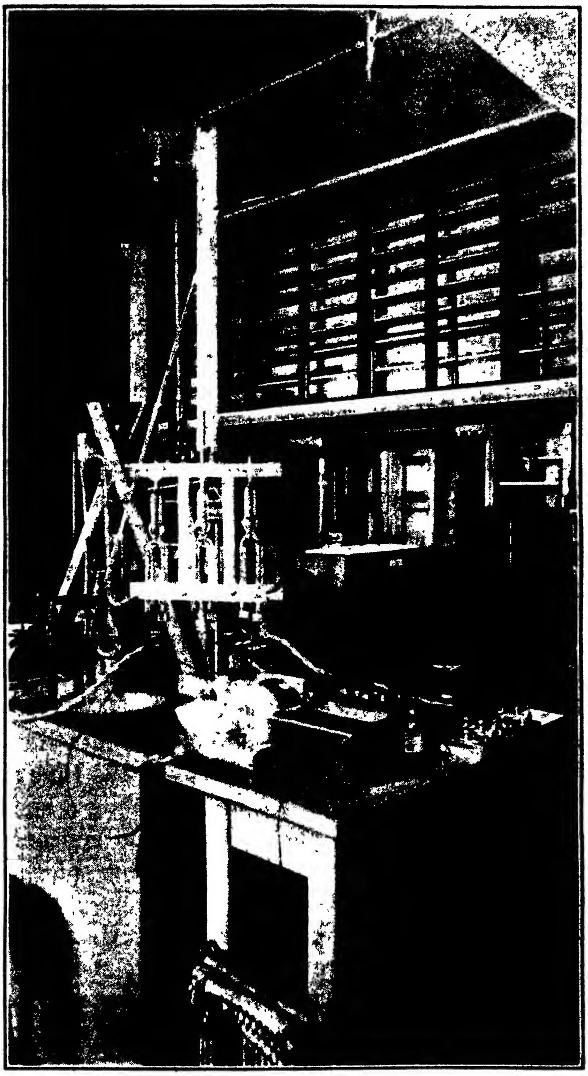


FIG. 17.—SECOND EXPERIMENTAL APPARATUS AS SET UP.

accurate one, and at the same time the improved apparatus affords a quantitative laboratory method—of special interest as no air solubility data seem to exist in other liquids than water—and one that also is easily utilized for industrial purposes in removing the gas content of a liquid.

As for Table 3, we have now evidently reached the desired effect, inasmuch as by far the largest air quantity is given off already by the separator *I*: the amount obtained in *III* is very insignificant. Further, the objection might possibly be made that some part of the gas obtained (and not analyzed) might be oxygen and hydrogen formed by electrolysis. However, in a separate experiment, it was established that one of the nichrome spirals in a dry condition had a resistance of 2.68 ohms, while when submerged in the water the resistance was found to be 2.677 ohms. If this difference is due to conduction in the water, it would in maximum give 0.2 cm.^{3} gas per liter, supposing a direct current had been used; as the current was alternating, this source of error may be entirely left out of account.

Conclusion

We have seen that the action of the hot wall in causing a local liberation of air from ordinary water on a hot-tube wall must be considered as an extremely important factor in corrosion—though of course a number of other factors may also be of influence. Nevertheless, the same action may be taken advantage of in order completely to remove the air from the water before it enters into the tube proper, thus preventing corrosion: *elementa suis armis devicta.*

The Ludwig-Soret Action

The central place in the foregoing investigations is marked by the phenomenon we have designated as the action of the hot wall. This action means that from an originally homogeneous solution a new phase is separated at points of a higher temperature. Now, the separation of a new phase generally implies the previous concentration of the component that is predominant in the new phase. We thus are led to the consideration of the action of the hot wall as being a special case of a much more general effect; *viz.*, the spontaneous concentration differences that may occur in a primarily homogeneous solution, when subjected to locally different temperatures.

This phenomenon was first discovered by C. Ludwig in Vienna in 1856. It received very little attention, however, and was rediscovered, in 1879, by C. Soret in Geneva—after whom it is generally called. J. H. van't Hoff, in 1887, ventured to give a theory of the phenomenon, which however, by an experimental investigation, S. Arrhenius (1898) has shown to be incorrect.[8] A demonstration apparatus of the phenomenon

[8] Van't Hoff (*Ztchr. f. phys. Chem.* (1887) **1**, 487) started from the assumption that the osmotic pressure must be the same in all parts of the solution. It appears to the author to be necessary instead to use as a starting point the fact that the thermodynamic potential, or the function ζ, which is dependent on concentration, temperature, and pressure, must be constant in different parts of a system.

was devised by R. Abegg (1898). The theory was improved by W. Duane (1898), and also by G. Tammann. In the laboratory of the latter, an experimental investigation was carried out by A. Eilert (1914). These references seem practically to comprise almost the entire original literature on the subject.

The reason why so little has been done is principally the great amount of time considered necessary in order to reach an equilibrium. Arrhenius spent 90 days for his experiment; in the work of Eilert, however, the time was reduced to about 20 hours.

The most interesting results obtained, as summarized by Eilert, are the following:

1. In a primarily homogeneous solution column subjected to a temperature gradient an equilibrium is finally obtained, inasmuch as the quotient of the concentration C_u in the cooled, lower part end the concentration C_o in the hotter, upper part, or $\frac{C_u}{C_o}$ becomes constant.

2. The quotient $\frac{C_u}{C_o}$ is always found to be greater than 1: *i. e.*, the solution is always found to have a higher concentration in the cold part than in the hot part.

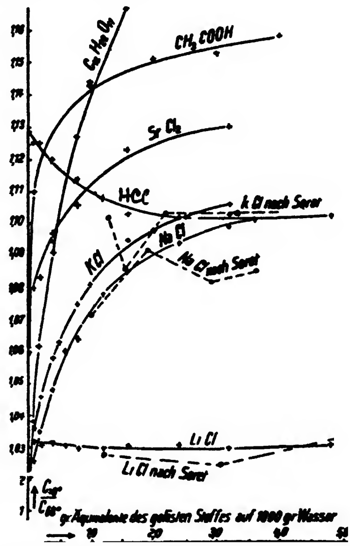


FIG. 18.—LUDWIG-SORET ACTION, ACCORDING TO EILERT.

3. The ratio $\frac{C_u}{C_o}$ increases nearly in all cases with the primary concentration of the solution; see Fig. 18 (Eilert). With decreasing concentration the ratio approaches to 100. For LiCl the ratio is constant, for HCl it decreases with increasing concentration.

4. As for water solutions containing LiCl, NaCl, KCl, and $SrCl_2$ respectively, the concentration ratio increases with the molecular weight of the solute.

5. The phenomenon does occur also in non-aqueous solvents, such as acetone and nitrobenzol.

This concentration change due to a temperature gradient having been proved to exist within ordinary liquids, it can not be denied that there is some probability of its existence likewise in molten alloys, though not observed—at least not directly—as yet. This gives the Ludwig-Soret phenomenon a certain interest for metallography. Before entering thereupon, we shall first examine somewhat more closely some of the results already referred to.

As stated under 2, the cold region of the solution has always been found to become the more concentrated one. From this, however, it seems to the author impossible to infer that the opposite may not likewise occur. As a matter of fact, let us suppose that there is a real tendency for the hot region to become more concentrated so that in a horizontal tube the hot part will be (say considerably) more concentrated. Now, suppose that the tube is turned in a vertical position with the hot end upwards, then the concentrated solution will probably descend to the bottom and it will appear as if there was a tendency for the cold portion to become more concentrated—which according to the assumption made is not the case.

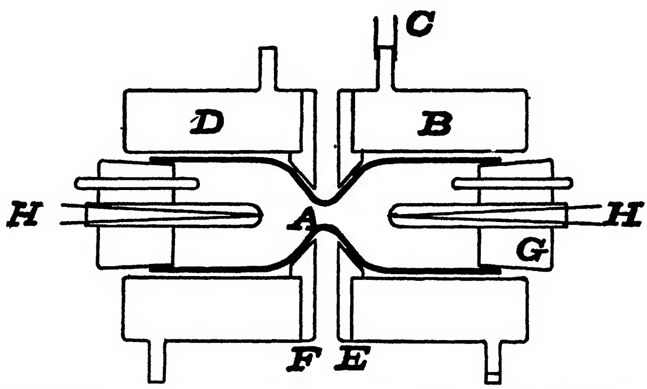


FIG. 19.—APPARATUS USED FOR STUDYING LUDWIG-SORET ACTION.

In order not to obtain results falsified by the action of gravity, the procedure would have to be thus: First, place the tube in a horizontal position; if it is found that—notwithstanding the convection currents—the hot part becomes more concentrated, the tube should be tilted gradually so that the hot end comes downward. Only in this way would it be possible to establish the paradoxical result: a stable equilibrium of the column, being hotter in the lower part than in the upper part. From these considerations it appears to the author to be indispensable to investigate in each case if, or how, gravity influences the Ludwig-Soret phenomenon. Some experiments, though by no means of a definite character, were carried out in this direction with the following method:

A glass tube *A* (Fig. 19) having an inner diameter of 18 mm. was strangulated in the middle to 5 mm. The right-hand portion was heated to +78° C. by means of a brass vessel *B* containing alcohol, which was kept boiling electrically; *C* is a tube for condensing the alcohol vapor. A cooling vessel *D* was kept at +16° C. by running water. By means of the split copper disks *E* and *F*, the temperature fall is localized to the middle portion of the tube. A rubber stop *G* is perforated by glass

tubing, which is intended for keeping a thermocouple and also for separating the two parts of the liquid, after an experiment—for which purpose the closed ends of H (and H') had a short rubber coating.

The strangulation permitted the experiments to be carried out in a horizontal position of the tube without much influence from convection currents; it obviously had the effect of lessening the diffusion speed. This, however, was not so serious an inconvenience, as even very small concentration differences could be accurately determined by means of an interferometer for liquids by C. Zeiss (construction F. Löwe).

The main experiment carried out was as follows: A sodium-chloride solution containing 20 gm. NaCl per 100 gm. H_2O—thus 3.43 normal—was heated as described, the apparatus being horizontal. After 52.5

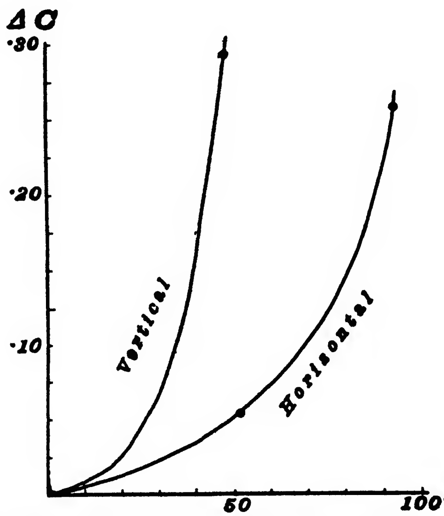


Fig. 20.—Influence of gravity on Ludwig-Soret action.

hr., the concentration difference was found to be 0.053 per cent. NaCl, the cold part being the more concentrated; after 93 hr. the difference was found to be 0.257 per cent.

The apparatus was then turned over into a vertical position with the heated part on top. After the lapse of 47.5 hr. the concentration difference was found to be 0.292 per cent. NaCl in favor of the lower part.

For the sake of comparison, these values are represented graphically in Fig. 20. It will be seen that there is considerable difference between the result obtained with a vertical position—as used by all previous workers—and a horizontal position: in the vertical position the speed of the concentration changes appear to be about six times greater than in the horizontal position. This does not prove that the final equilibria

will differ in the same way,[9] but it appears highly probable that the Ludwig-Soret phenomenon as determined so far is affected by gravity in an unmistakable manner, not before taken into consideration.

It is interesting to compare this conclusion with the result mentioned as 4, page 617; *viz.*, that the concentration at the lower part of the vessel has been found to increase with the atomic weight of the solute.

In addition to this, we also might consider that Eilert, for chloride of lithium, found a concentration ratio in acetone (specific gravity 0.80) considerably greater than in water, and for acetic acid a ratio in water considerably greater than in nitrobenzol (specific gravity 1.20). Thus, the lighter the solvent, the greater is the tendency of the solute to sink to the lower part of the vessel. It appears doubtful whether the same will be true in case the determinations are made independent of gravity, and whether the cooler solution thus always will be found to be the more concentrated.

In one experiment carried out with the foregoing apparatus (horizontal) on a solution containing 30 gm. $MgSO_4$ per 100 gm. H_2O, after a lapse of 42 hr., it was found that the portion which has been heated had a concentration slightly greater than the colder portion; the difference however was only 0.35 drum divisions of the interferometer and evaluated in per cent. was very insignificant.

Because of the results now reached, this work will be pursued with a modified method. However, we may already conclude that the position reached by previous workers—the cooler portion gets the higher concentration—may not be a general law.

Segregation in Molten Iron, Occurring Previous to Solidification

A Swedish metallurgist some time ago asked the author for an explanation of his unexpected result in finding a higher carbon content in the outer layer of some large ingots than in the interior. The metal being gray iron, the author's first answer was to suggest errors in analysis, due to a systematic graphite loss. A number of careful control analyses having then been made, the former result was corroborated. This induced the author to consider the question of segregation from a wider point of view than that generally taken.

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[9] The values found here are much lower than those found by the previous workers. Thus, in the last case a concentration quotient was found of

$$\frac{20.00 + \frac{1}{2} \cdot 0.292}{20.00 - \frac{1}{2} \cdot 0.292} = 1.013$$

while Eilert using sensibly the same temperature difference and solution found an equilibrium quotient amounting to 1.071. This difference is obviously due to the strangulation of the vessel used here, permitting horizontal work but necessitating a much prolonged duration of time.

As a matter of fact, segregation since the earliest times has been a very obscure phenomenon, until the phase rule and the whole doctrine of heterogeneous equilibrium gave us the explanation of its most striking characteristics. So the fact that in a mild steel a concentration of carbon nearly always occurs in the last solidifying portion, as well known, is directly explained on considering the change in the heterogeneous equilibrium as evidenced by the solidification diagrams. (It is true that exceptions from the regular segregation behavior as predicted by these diagrams might occur as the result of gases liberated during the course of the solidification; of course, this item is not considered in the diagrams.) Nevertheless, there are some characteristics of segregation that, so far as the author knows, have not received any elucidation. Before briefly referring to this aspect of segregation let us at once state that a solidification diagram is only the expression of the heterogeneous equilibrium—the equilibrium between the phases—of a system, presupposed to have a uniform temperature all over.

On the contrary, the thermal diagram as hitherto given expresses nothing regarding the homogeneous equilibrium, or for the equilibrium of a homogeneous phase parts of which have different temperatures.

Hence, if we find that the composition of a homogeneous phase, when subjected to a temperature gradient, is locally changed; or, in other words, if we find the Ludwig-Soret phenomenon to be valid likewise for metallic phases, this will stand in no opposition to the existing diagram of thermal equilibrium, it will only signify a supplementing of them.

Dealing with segregation, it is natural first to consult the work by H. M. Howe. In his "Metallurgy of Steel" (1890), Howe refers to an investigation of Maitland (1887) summed up in a diagram (Fig. 80) which gives the carbon content at different points in the vertical section of a large ingot. This is reproduced in Fig. 21. The inner part of the ingot (corresponding to five vertical columns), where the solidification has been quite slow, well illustrates the segregation as explained by the equilibrium diagram (later established): the lower end of the interior has a very low carbon content (about 0.23 per cent.); this increases successively in the upper parts—which have solidified later—so as to reach a high value near the top (about 0.7 per cent.). This interior part, however, is surrounded by an outward layer which, on account of the cooling effect of the mold, must have solidified much more quickly than the interior; it thus must better represent the concentration state before beginning solidification. Now, in this outer part of the ingot, a slight increase in the carbon content is to be found when progressing from the top to the lower part (mean value of the lower half part of the first column is 0.320 per cent., of the upper part 0.287 per cent.).

In his later book "Iron, Steel and Other Alloys" (1903), where the same figure is reproduced, Howe refers to an "abnormal segregation" in

cupriferous silver. "The explanation of this phenomenon does not seem clear. Convection currents and gravity stratification of the nascent solid constituents in the act of freezing may contribute."

An exhaustive investigation on segregation in steel ingots is that of B. Talbot. In the outside portion of a large ingot (6000 lb. or 2721 kg.) he found the following figures.

Points	1 (top)	2	3	4	5	6	7	8	9	10	11	12 (bottom)
Carbon content	33	32	31	32	35	37	38	38	36	38	41	43

This unmistakably indicates that the carbon content in the outer part increases toward the bottom; this segregation, however, does not occur in the case of aluminum addition before pouring.

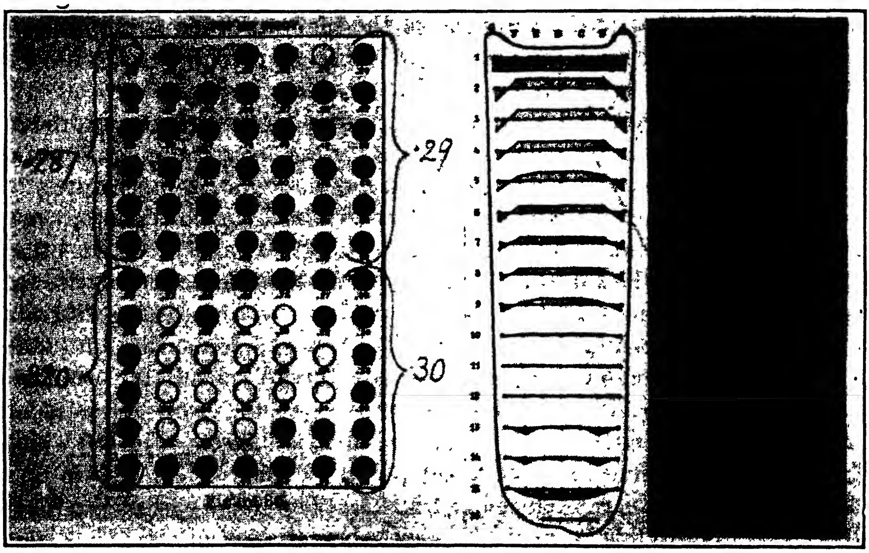

FIG. 21. FIG. 22.

FIG. 21.—SEGREGATION IN A LARGE INGOT, ACCORDING TO MAITLAND AND HOWE. PERCENTAGE OF CARBON AT DIFFERENT POINTS IN VERTICAL SECTION OF A LARGE INGOT; DEPTH OF SHADING OF SPOTS IS ROUGHLY PROPORTIONAL TO PROPORTION OF CARBON.

FIG. 22.—DISTRIBUTION OF CARBON IN A LARGE STEEL INGOT, ACCORDING TO BERGLUND.

A number of valuable papers on segregation have been published by P. H. Dudley (1913), R. A. Hadfield (1912), H. M. Howe (1907) P. Oberhoffer (1920), B. Osann (1912), A. Pourcel (1893), J. E. Stead (1906), A. Wahlberg (1901), F. Wüst and H. L. Felser (1910), and many others; and due attention to the matter is paid in the textbooks as in those of F. W. Harbord and J. W. Hall, B. Osann, H. Wedding, without throwing much light on the kind of segregation we are studying. However, a careful scrutiny of a 0.19 per cent. steel ingot has been made quite

recently by T. Berglund (1923) at the School of Mines in Stockholm. The distribution of carbon is clearly shown, the algebraic differences from the mean value being taken as vertical coördinates at each of the 109 points analyzed; see Fig. 22. The result is a very regular one; a similar, regular distribution was obtained also for phosphorus and sulfur.

The interior part (clearly marked by blowholes) has a carbon content low at the bottom (0.16 per cent.) and increasing (to 0.21 per cent.) near the top. The outer part, on the contrary, has a carbon content of 0.19 per cent. at the bottom and decreases regularly to 0.15 per cent. at the top.

This result constitutes a valuable corroboration of the earlier ones, already referred to, and is borne out by the fact that Berglund, like previous workers, found sulfur and phosphorus to vary essentially in the same way.

Assuming accordingly the distribution as thus found to represent the general rule we are justified in saying: The segregation of the interior of a large ingot, giving the highest carbon content near the top, is essentially explained by the diagram of heterogeneous equilibrium, assuming the freezing to progress from the bottom part. The concentration differences of the outer part, on the contrary, showing the highest carbon content at the bottom, cannot be explained by this heterogeneous diagram but affords a strong evidence in favor of a Ludwig-Soret effect, occurring in the molten iron containing a low carbon content.[10]

Regarding higher carbon contents, a few isolated segregation data are available. So Osann,[11] in his "Lehrbuch der Eisen und Stahlgiesserei" refers to a pig-iron analysis quoted by Ledebur:

	C, Per Cent.	Si, Per Cent.	Mn, Per Cent.	P, Per Cent.	S, Per Cent.	Cu, Per Cent.
Outer part	3.97	3.65	1.58	0.02	0.03	0.04
Inner part	3.41	3.68	1.32	0.01	0.02	0.03

Thus a decided carbon surplus was found in the cooler outer part. It seems, however, scarcely possible to draw any definite conclusion from a few isolated figures. The author, therefore, values the opportunity, afforded him by the courtesy of the Surahammars Bruks Aktiebolag, Sweden, of presenting here some data, being the result of an elaborate investigation made by G. Malmberg, at Surahammar.

A section had been obtained from a large cast-iron roll (weight about 20 tons). Carbon and phosphorus were determined with the greatest possible care, especially so as to avoid any error due to graphite loss, on

[10] As pointed out to the author by B. Kjerrman, the tar generally used in the molds might influence the carbon distribution; this, however, is not very probable, as phosphorus and sulfur are subjected to similar changes as carbon.

[11] At the same place Osann quotes a case of segregation observed by Reusch in a roll, cast in bessemer steel: upper neck, 0.215 per cent. carbon; body of roll, 0.309 per cent. carbon; lower neck, 0.314 per cent. carbon.

20 points at different distances d from the surface. The result, as communicated by Mr. Malmberg, has been reproduced graphically as a function of d in Fig. 23. Making allowances for unavoidable local differences in composition, we see that the carbon content, 3.62 per cent. at the surface, decreases quite considerably toward the center of the roll; this differentiation in carbon content seems to have no connection with the fact that the outer zone (about 30 mm.) is white, while the interior is gray. Further, the same holds true for the phosphorus content, which in

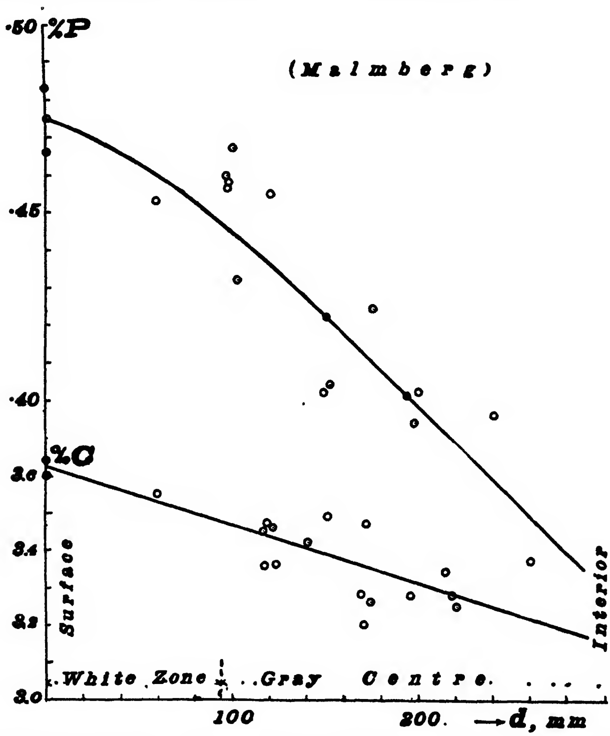

FIG. 23.—DISTRIBUTION OF CARBON AND PHOSPHORUS AS A FUNCTION OF THE DISTANCE d FROM THE SURFACE OF A LARGE INGOT, ACCORDING TO MALMBERG.

a slightly more irregular way decreases from about 0.475 per cent. at the surface, to below 0.40 per cent. near the center. Thus, as was already found by the determinations at a low-carbon content, a remarkable carbon segregation occurs—the carbon content increasing when progressing with the temperature gradient which must have existed previous to solidification. The direction of this segregation, as in the earlier cases, is the opposite to the direction of segregation that may be deduced from the heterogeneous equilibrium diagram.

It might be supposed that the lowering of the carbon content toward the center might be due to some considerable amount of carbon being

ejected from the still liquid portion of the metal, as graphite flakes ("kish"). This explanation, however, would be contrary to the equilibrium diagram, as this separation of graphite from the molten metal demands a total carbon content slightly surpassing 4.0 per cent. (the eutectic content being near 4.07 per cent.[12]), while the present carbon content is much lower. Furthermore, the phosphorus segregation evidently could not be explained by that supposition.

Conclusion

From the foregoing facts, we conclude that the particular form of segregation in molten iron which implies a concentration of carbon toward the cooler portions—being apparently contrary to the heterogeneous equilibrium diagram—is due to Ludwig-Soret phenomenon occurring likewise in the domain of alloys; in this effect, as we have seen, a concentration of the solute to the cold portion is the only case hitherto observed.

Ludwig-Soret Action in Various Alloys

From the foregoing it is natural to infer that the Ludwig-Soret phenomenon also occurs in molten metals (salts and so forth) in general. The wide field that in this way is opened for metallographic investigation has so far only been approached by the author and his collaborators. It may be mentioned here, however, that considerable concentration changes have been found in some determinations made by Mr. P. Sederholm, in the case of bismuth-tin alloys, kept throughout in the liquid state. An experiment, carried out by S. Wässman had given a considerable concentration difference in molten steel; the results, however, being strongly affected by oxidation, are not conclusive.

It is well known to every mining engineer that in geology the problem of magmatic differentiation, or the formation of differences of concentration in a silicate magma, has been the object of much discussion. From the facts now dealt with, especially those concerning liquid alloys, we are induced to draw the conclusion that this differentiation, in so far as it concerns a completely liquid magma, must depend to a very considerable degree on a generalized Ludwig-Soret action.

On consulting the geological literature, one finds that this point of view is not new. It has been proposed by J. J. H. Teall (1886–88), A. Lagorio (1887), and W. C. Brögger.[13] On the other hand, petrographers have expressed the opinion that "Soret's principle cannot be applied to magmas;"[14] more recently, in discussing the subject, Bowen[15] came to

[12] C. Benedicks: "*Metallurgie*" (1906) **3**.

[13] J. H. Vogt: *Geol. Fören. Förhandl.* (1891) **13**, 476.

[14] H. Bäckström: *Jnl. of Geol.* (1893) **1**, 773.

[15] N. L. Bowen: *Jnl. of Geol.* (1915) **23** (Supplement to No. 8), 1. I am indebted to Prof. P. Quensel for referring to this paper.

the conclusion that the Soret effect, in the case of magmas, would be quite negligible.

It is not possible for me to share this opinion—though it seems at present to be the prevalent one among geologists. As a matter of fact, the experimental items treated in this lecture, especially the segregation in large ingots, decidedly support the view that the magmatic differentiation cannot be fully investigated—just as is the case with the metallic segregation—without due consideration of the Ludwig-Soret action. It is quite obvious that at comparatively low temperatures, near the freezing range of the magma, its influence must be weak as compared to the differentiation due to crystallization; on the contrary, at much earlier periods with a considerably higher temperature of the magma, its influence presumably has been a very marked, regional one.

The general influence of the generalized Ludwig-Soret phenomenon thus might exert a marked influence on this planet, in its entirety, and possibly also on other stellar bodies.

I hope in this lecture to have succeeded to some extent in illustrating that research, even when dealing with prosy problems of immediate practical interest—as that corrosion of boiler tubes cannot afford to dispense with the practical aid of abstract science; and on the other hand that pure science can scarcely finds its full development without contact with the practical problems of life.

Recrystallization and Grain Growth in Soft Metals

By Maurice Cook, M. Sc., Ph. D., and Ulick R. Evans, M. A., Cambridge, England

(New York Meeting, February, 1925)

The structural changes in metals brought about by annealing following a deformation at a low temperature has been the subject of many investigations. No less than eleven metals and alloys have been studied in some detail; namely, aluminum,[1] tungsten,[2] iron,[3] copper,[4] gold,[5] zinc,[6] cadmium,[7] tin,[8] lead,[9] brass,[10] and cupronickel.[11] As a result, it is possible to frame a qualitative statement of the effect of the degree of deformation and the temperature of annealing on the structure finally attained.

[1] H. C. H. Carpenter and C. F. Elam: *Jnl.* Inst. Met. (1921) **25**, 259.
E. Rassow and L. Velde: *Ztschr. Metall.* (1921) **13**, 557.

[2] Z. Jeffries: *Jnl.* Inst. Met. (1918) **20**, 124.
C. J. Smithells: *Trans.* Faraday Soc. (1922) **17**, 485; *Jnl.* Inst. Met. (1922) **27**, 107.

[3] C. Chappell: *Jnl.* Iron and Steel Inst. (1914) **89**, 460.
R. H. Sherry: *Trans.* Faraday Soc. (1916–17) **12**, 284.
A. E. White and H. F. Wood: *Proc.* Am. Soc. Test. Mat. (1916) **16**, Part II, 82.
A. Sauveur: Int. Ass. Test. Mat. 6th Congress (1912) First Section, Part II, 6.

[4] E. Rassow and L. Velde: *Ztschr. Metall.* (1920) **12**, 369. See also the work of Grard, described by L. Guillet and A. Portevin, "Introduction to the Study of Metallography and Macrography."

[5] T. K. Rose: *Jnl.* Inst. Met. (1912) **8**, 107.

[6] G. Timoféef: *Rev. Met.* (1914) **11**, 127; *Compt. Rend.* (1912) **155**, 430.
G. Masing: *Ztschr. Metall.* (1921) **13**, 425.

[7] M. Cook, *Jnl.* Inst. Met. (1923) **29**, 119.
J. N. Greenwood: *Trans.* Faraday Soc. (1922) **17**, 681.

[8] G. Masing: *Ztschr. Metall.* (1920) **12**, 457.
J. Czochralski: *Int. Ztschr. Met.* (1916) **8**, 1. Compare the work on tin containing antimony by H. C. H. Carpenter and C. F. Elam: *Jnl.* Inst. Met. (1920) **24**, 83.

[9] J. A. Ewing and W. Rosenhain: *Phil. Trans.* [A] (1900) **195**, 284.

[10] C. H. Mathewson and A. Phillips: *Trans.* (1916) **54**, 608.
F. G. Smith: *Trans.* (1920) **64**, 159.

[11] F. Adcock: *Jnl.* Inst. Met. (1922) **27**, 73.

Effect of Degree of Deformation

It appears to be a universal rule that the smaller the amount of deformation has been, the larger the grain size produced on annealing, provided always that the temperature of annealing is sufficiently high, and the time allowed is sufficiently long, for the structural changes to complete themselves. The reason is probably as follows: Deformation involves a passage from a stable to an unstable state, so it is natural to suppose that when the temperature is raised sufficiently, the atoms in the disorganized regions will commence to rearrange themselves in a manner representing a greater degree of stability. The most disorganized regions—according to the ordinary ideas of gliding—will be the crystal boundaries and the gliding planes. It is significant that in both aluminum[12] and copper,[13] the crystals produced on annealing appear first at the grain boundaries and grow out most readily along the direction of the boundaries; while in cupronickel,[14] the new crystals seem to be formed preferentially along the gliding planes and grow most rapidly in the direction of those planes. The greater the amount of disorganized matter in a specimen, the greater is the number of grain nuclei that will be formed in unit volume; in other words, the greater the deformation, the smaller the final grain size. As already stated, this is found to be the case.

But the changes that occur on annealing do not consist only in the formation of fresh grains from nuclei (recrystallization); some of the old grains grow at the expense of their neighbors. Carpenter and Elam[15] think that it is the deformed crystals which grow at the expense of the less deformed. As pointed out by one of the present authors,[16] this view appears to be inconsistent with the generally accepted principles of crystallization and of heterogeneous changes generally. The stable phase will always tend to expand at the expense of the metastable phase; if ice and water are in contact below 0° C., the ice will grow into the water, not the water into the ice. The suggestion was put forward, therefore, that it is the least deformed grains that grow; this view has since received support from Smithells.[17]

Various other views have been expressed regarding the factors determining which grains shall grow at the expense of others. Jeffries[18] has asserted that the larger grains will tend to consume the small ones.

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[12] H. C. H. Carpenter and C. F. Elam: *Jnl.* Inst. Met. (1921) **25**, 269.

[13] E. Rassow and L. Velde: *Ztschr. Metall.* (1920) **12**, 369.

[14] F. Adcock: *Jnl.* Inst. Met. (1922) **27**, 73.

[15] H. C. H. Carpenter and C. F. Elam: *Jnl.* Inst. Met. (1920) **24**, 83.

[16] U. R. Evans: *Jnl.* Inst. Met. (1921) **25**, 299. See also reply to this criticism by H. C. H. Carpenter and C. F. Elam: *Proc.* Roy. Soc. [A] (1922) **100**, 351.

[17] C. J. Smithells: *Jnl.* Inst. Met. (1922) **27**, 125

[18] Z. Jeffries: *Jnl.* Inst. Met. (1918) **20**, 116.

Smithells[19] has expressed a similar view, quoting the thermodynamical work of Pawlow[20] to show that the big grains must grow and the small ones must perish. But Pawlow's argument, if it is applicable at all, would lead to the view[21] that the grains with small (convex) curvature should grow at the expense of those with great curvature; this does not necessarily mean that the large grains consume the small ones, unless the grains are spherical.

The thermodynamical argument, however, did lead to the suggestion[22] that "where the boundary between two grains was curved, the grain on the concave side would tend to grow into the grain on the convex side, thus reducing the interfacial energy of the system." This prediction recently received experimental confirmation by the work of Vogel.[23]

Other views of the mechanism of grain growth after deformation have been put forward. Tammann[24] thinks that even in the purest specimens of metal obtainable, a thin film of impurities exists between the grains, isolating them from one another; the function of deformation is to break down this film and bring the grains into real contact with one another, thus allowing recrystallization or grain growth to take place. It is undeniable that the presence of impurities that constitute a separate phase (for instance, thoria in tungsten,[25] and iron carbide in iron[26]) do hinder grain growth. But it seems highly improbable[27] that a film of intergranular impurities really exists in the purest samples of most metals; certainly it is difficult to picture this film as being so continuous and perfect as to isolate the crystals from one another. Furthermore, it has been pointed out by Alterthum[28] that in polycrystalline specimens obtained by the recrystallization of originally monocrystalline specimens, the grains can exist in contact with one another at high temperature without growth; clearly, in such cases the existence of a film of impurities is excluded.

It is important to notice that although at moderately low temperatures changes only occur in metals that have received mechanical deformation, it has been shown[29] that cast cadmium subjected to no mechanical stresses other than the slight stresses inseparable from casting shows

[19] C. J. Smithells: *Jnl.* Inst. Met. (1922) **27**, 128.
[20] P. Pawlow: *Ztschr. Phys. Chem.* (1908) **65**, 1.
[21] U. R. Evans: *Jnl.* Inst. Met. (1922) **27**, 139.
[22] U. R. Evans: *Jnl.* Inst. Met. (1922) **27**, 140.
[23] R. Vogel: *Ztschr. Anorg. Chem.* (1923) **126**, 5.
[24] G. Tammann: *Ztschr. Anorg. Chem.* (1920) **113**, 163, especially pages 166, 174.
[25] C. J. Smithells: *Jnl.* Inst. Met. (1922) **27**, 118.
[26] C. Chappell: *Jnl.* Iron and Steel Inst. (1914) **89**, 489.
[27] M. Cook: *Trans.* Faraday Soc. (1923) **19**, 47.
[28] H. Alterthum: *Ztschr. Metall.* (1922) **14**, 422.
[29] M. Cook: *Trans.* Faraday Soc. (1923) **19**, 43.

marked coarsening of structure if subjected to a long annealing at a temperature a little below the melting point.

A similar change appears to take place in gold. Fraenkel[30] heated gold at 1045° C. for 45 min., and published photographs showing the grain boundaries before and after the anneal. As the old grain boundaries were visible, after the anneal, in the same position, Fraenkel drew the conclusion that no change had occurred. But closer examination of the photomicrograph reveals that one grain at least has been invaded by its four neighbors, the new boundaries being shown by well-defined lines.[31] It has also been stated by Sauerwald[32] that grain growth can take place when metallic powders are heated, even where the method of preparation has been such as to exclude deformation.

Another case where recrystallization occurs without mechanical stress is in the annealing of cored solid solutions, such as α-brass. Observations[33] have indicated that "one dendrite can give rise to more than one polygonal grain, and also that several dendrites may ultimately be merged into only one grain." This view has received confirmation from subsequent x-ray work by Bain.[34]

Effect of Annealing Temperature

The temperature needed to produce appreciable change in a deformed metal is higher if the deformation is slight than if the deformation is great. Consequently, if an article that has been deformed more in certain parts than in others is annealed, the least deformed parts will, in general, escape change. If the annealing temperature is low, only the most highly deformed region will become recrystallized; if, however, the temperature is high, the change will extend farther into the regions of comparatively low deformation and, on account of this fact, a zone of very large grains will be produced.[35]

In the annealing of a uniformly deformed specimen, the elevation of the annealing temperature may operate in two ways: (1) It will increase the number of nuclei formed in unit volume in unit time (Tammann's Kernzahl or K.Z.); this will tend to decrease the grain size; (2) it will tend to increase the velocity of crystallization (Tammann's Kristallisation-Geschwindigkeit or K.G.) which, by causing the first-formed grains to extend and meet one another before fresh ones can be formed, will clearly

[30] W. Fraenkel: *Ztschr. Anorg. Chem.* (1922) **122**, 295.

[31] M. Cook: *Trans.* Faraday Soc. (1923) **19**, 48, 51; U. R. Evans: *Trans.* Faraday Soc. (1923) **19**, 50.

[32] F. Sauerwald: *Ztschr. Anorg. Chem.* (1922) **122**, 277.

[33] M. Cook: *Trans.* Faraday Soc. (1922) **17**, 522.

[34] E. C. Bain: *Chem. & Met. Eng.* (1923) **28**, 66.

[35] C. Chappell: *Jnl.* Iron and Steel Inst. (1914) **89**, 477; D. Hanson: *Jnl.* Inst. Met. (1918) **20**, 141.

have the opposite effect.[36] It is impossible to predict which of these two factors will prevail. Actually, the experimental evidence available appears to show that in copper, [37] brass,[38] and tin [39] a high annealing temperature usually causes a coarser grain than a low temperature; according to Timoféef[40] the same rule holds good for zinc, but Masing[41] has shown that under certain conditions a high temperature may produce a smaller grain size in zinc than a low temperature. In aluminum, also, Carpenter and Elam[42] have shown that under certain conditions a high annealing temperature causes a much finer grain than a lower temperature; in fact, their well-known method of producing monocrystalline specimens[43] consists essentially in heating the specimens so slowly that the change is completed at the lowest temperature possible. Jeffries[44] cites numerous cases of the production of abnormally coarse grains when a piece of metal is heated to what he calls the "germinative temperature," that is, the temperature just high enough to produce growth at a few, but only a few, points.

The temperature required to cause recrystallization depends not only on the deformation but on the nature of the metal. For hard metals, a comparatively high temperature is required; but for soft metals, in which the natural restraint on atomic movement is less, the rearrangement of atoms in stable crystal array occurs at a lower temperature. Very soft metals, such as lead, are usually held to be "self annealing;" that is, after deformation they sometimes undergo annealing spontaneously at ordinary temperature. This matter will be referred to later in this paper.

Need for a Statistical Study

In most of the work hitherto conducted on grain growth and recrystallization, the investigators have taken photomicrographs of the metals at different stages of annealing and, by studying these, have arrived at a general impression of the changes in progress. Often the fortunes of individual grains have been followed through several stages; but it is doubtful whether in any research the numbers studied have been sufficient for applying even roughly a statistical method. The method of "general

[36] H. Alterthum: *Ztschr. Elektrochem.* (1922) **28,** 347, appears to have neglected this factor.

[37] E. Rassow and L. Velde: *Ztschr. Metall.* (1920) **12,** 369.

[38] C. H. Mathewson and A. Phillips: *Trans.* (1916) **54,** 640.

[39] J. Czochralski: *Int. Ztschr. Met.* (1916) **8,** 1.

[40] G. Timoféef: *Compt. Rend.* (1912) **155,** 430; *Rev. Met.* (1914) **11,** 127.

[41] G. Masing: *Ztschr. Metall.* (1921) **13,** 425.

[42] H. C. H. Carpenter and C. F. Elam: *Jnl.* Inst. Met. (1920) **24,** 124.

[43] H. C. H. Carpenter and C. F. Elam: *Proc.* Roy. Soc. [A] (1921) **100,** 333.

[44] Z. Jeffries: *Trans.* (1916) **54,** 658.

impressions" has undoubtedly led to the discovery of many of the fundamental truths; but where the general impressions of different investigators do not agree, it is impossible to decide the point at issue without recourse to a statistical method. The investigation described in this paper was primarily an attempt to obtain some statistics regarding the frequency of the different modes of change in lead; a certain amount of work was also conducted on tin and cadmium.

Method of Carrying Out the Metallographical Operations

Materials Employed

The lead used in these researches was Cookson's "superfine metallic lead," and was presented to the authors by Messrs. William Jacks & Co.; we take this opportunity of expressing our thanks for their kindness. It contained over 99.99 per cent. of lead; even after the casting and rolling operations, the iron content was found to be well below 0.01 per cent.; there was a trace of arsenic. The cadmium contained 0.07 per cent. lead and 0.08 per cent. iron. The tin contained a trace of arsenic and iron.

Preliminary Treatment

The metals were cast into slabs 11 by 2.5 by 0.7 cm. in an iron mold, and then rolled down to strips 2.5 mm. thick. These were cut into suitable lengths (usually 7 to 8 cm.), stamped with distinguishing letters, pressed flat (if necessary) between sheet celluloid held between wooden blocks in the jaws of a vise, and annealed at 180° C. for 30 to 60 min. The surface of the specimens, when etched, showed a good polygonal structure, which will be referred to as the "preliminary structure," see Figs. 3, 4, and 5. The grain size of the lead is coarser than that of tin; which, in turn, is coarser than that of cadmium. The grains in tin and cadmium were more uniform in size than those in lead.

The advantage of obtaining a smooth surface without polishing is very great. The cold work necessarily involved in polishing would have caused disastrous complications in interpreting the results. Furthermore, the practical difficulties of polishing a soft metal without obliterating the structure are considerable.

Etching

For lead, the etching solution that proved most suitable contained 100 c.c. of 10 per cent. nitric acid and 6 drops of 20 per cent. chromic acid.

The specimen was immersed in the solution, in a porcelain dish, rubbed gently with a camel's hair brush until the desired effect was obtained, then washed with water, then with 10 per cent. nitric acid,

and again with water. After this, it was soaked in alcohol for a few minutes and rapidly dried with a soft handkerchief, the last remaining film of alcohol being allowed to evaporate in air.

For cadmium the same etching solution diluted with an equal part of water was found to be suitable.

For tin, in the case of the rolled specimens in the early stages of annealing, immersion in strong hydrochloric acid for a few seconds was needed to develop the structure; this was followed by a longer immersion in dilute hydrochloric acid (1 part concentrated acid in 5 parts water) to which a small amount of ferric chloride had been added, in accordance with the plan of Heycock and Neville.[45] In the advanced stages of annealing, the immersion in concentrated hydrochloric acid, which was apt to produce a rather rugged, pitted appearance, could often be omitted.

Marking of Areas

As it was desired to photograph the same area at different stages of the anneal, it was necessary to have some sure means of identifying the area. Definition of an area by scratching or by pinholes was unsatisfactory because of the risk of deformation being produced. Consequently a special marking tool was made by pinching a cork-borer to such a form that it left a pear-shaped mark of the desired size when pressed gently on to the lead surface. When the specimen was placed on the

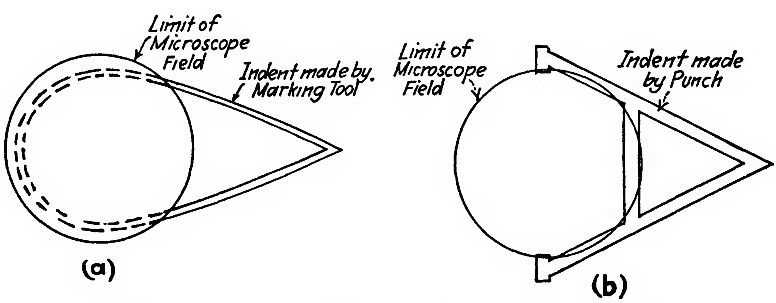


FIG. 1.—ADJUSTMENT OF MARKS TO MICROSCOPIC FIELD.

microscope stage, it was adjusted so that the rounded end of the impression just fitted into the circle of the microscope field as indicated in Fig. 1 (*a*). A specimen marked with this tool is shown in Fig. 11.

It was found that when the tool was gently pressed on to lead, the indentation involved so little deformation that no recrystallization or grain growth occurred in the area (except actually in the mark produced by the tool) on annealing at 200° C. Deeper marking was intentionally used in some cases, where a local deformation was desired. In experi-

[45] C. T. Heycock and F. H. Neville: *Phil. Trans.* [A] (1903) **202**, 17.

ments where the specimen was subsequently to undergo severe rolling, a comparatively deep mark was always required, so as to avoid obliteration; in such cases, it was considered safest to mark the specimens before the preliminary anneal.

With tin, this method was not satisfactory, and the areas under observation were defined with reference to the letters stamped on the specimen before the preliminary anneal. Thus, an area could be identified by allowing the two prongs of the letter A to appear just on the edge of the specimen, as shown in Fig. 1 (*b*).

Photography

It is common practice in metallography to obtain photomicrographs of specimens illuminated by vertical light. This method gives excellent results with alloys, and even on simple metals good results are often obtained, especially if they have been etched in such a way as to produce dark boundary lines between the grains, or where the grains themselves are covered with twin bands or slip bands. The method does not prove so satisfactory, however, in developing simple polygonal structure

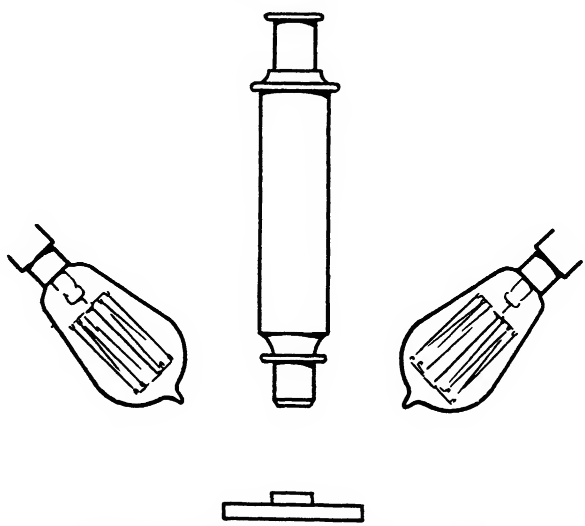


FIG. 2.—GENERAL OBLIQUE ILLUMINATION.

in a fully etched metal; for, when all the incident rays are nearly parallel to one another, the probability of the reflection of the light up the microscope tube by a given grain is very small; consequently while here and there a grain appears brilliantly white, most of the grains appear black or nearly black. If, however, the light strikes the specimen at all sorts of angles, the probability that a given grain may reflect an appreciable amount of light up the tube is greatly increased. It is not desirable, of


FIG. 3.—LEAD, PRELIMINARY STRUCTURE. × 50.

FIG. 4.—TIN, PRELIMINARY STRUCTURE. × 50.

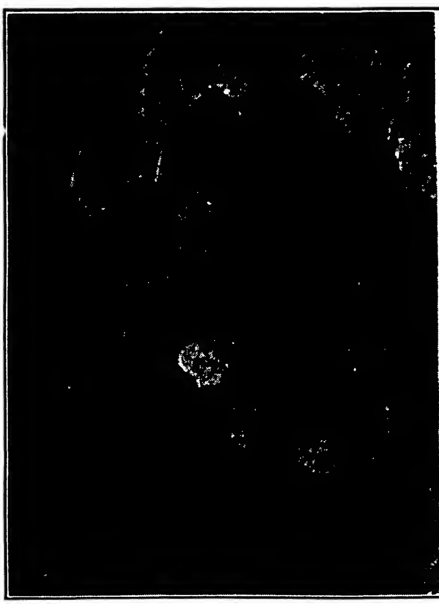
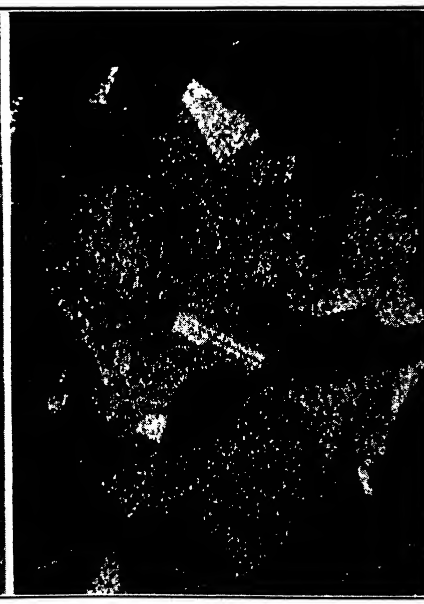



FIG. 5.—CADMIUM, PRELIMINARY STRUCTURE. × 50.

FIG. 6.—LEAD, DEEPLY ETCHED. × 50.

course, to have light arrive at every angle, as this would render every grain bright.

It was found that if two electric lamps (40 watts) were placed above the specimen, one on each side of the tube, as shown in Fig. 2, a satisfactory distribution of light and shade was obtained. Some grains appeared white, some light gray, some dark gray, and some black. In several cases, what appeared under vertical illumination to be one large dark grain, by this method of general oblique illumination was shown to be a group of two or more grains. The photomicrographs shown in Figs. 3, 4, and 5 were obtained by this method.

Our observations led us to believe that the reflection which causes certain grains to appear light comes mainly from a series of etching pits with which the surface becomes "peppered." Certain grains that, to the naked eye, appeared uniformly white, when examined under a microscope, were found to owe their brightness to the presence of numerous etching pits, which reflected light strongly, the grain itself being dark. The neighboring grains, which appeared dark to the naked eye, either contained fewer etching pits, or pits that (because of their smaller size or the different inclination of their facets) did not reflect much light. This is illustrated in Fig. 6, which shows a rather deeply etched surface of lead. It is to be expected that the frequency and size of the pits in different grains, as well as the inclination of the facets, should be affected by the angle that the crystallographic axes make with the surface of the specimen.

Deformation

As already stated, the "marking tool" was employed in some cases to produce deformation in the metallic specimens. In cases where a quantitative measure of deformation was desired, the method of rolling was always used. The length of the specimen was measured, and it was then passed through the rolls until a certain percentage of elongation was produced; care was taken that the specimen should be pulled through the rolls rather than pushed through them, so as to avoid undue bending. Measurements of the thickness with a micrometer before and after rolling showed that the decrease in thickness corresponded closely to the increase in length.

Annealing

For the preliminary annealing, an ordinary air bath was generally used; while for much of the work, in which it was merely desired to follow the fortunes of individual grains, a small electric oven was used. In the experiments designed to determine the range of temperature at which recrystallization, or grain growth, began to show itself in different cases, the specimens were packed in asbestos fiber in a copper box lined with

asbestos and fitted with an asbestos cover. The box was covered with asbestos below and at the points where it would approach most nearly to the walls of the oven, and was then supported on fireclay stands placed on the floor of an air oven. Two thermometers passing through the asbestos cover, so that the bulbs were placed among the specimens, allowed the temperature to be recorded in different parts of the box.

In certain cases, it was important that the specimens should be brought quickly to a given temperature. Direct heating of the specimens in a bath of high-boiling paraffin or aniline was then employed. The bath was heated a few degrees higher than the temperature aimed at, and the specimens were plunged in and the liquid stirred. The thermometer quickly fell and, by observing when this rapid fall ended, it was possible to get an idea as to the time needed for the specimens to reach the temperature desired. It was found that the specimens came within a few degrees of the annealing temperature in a few seconds, and that after half a minute they might be considered to be at the temperature of the bath.

Statistics of Births, Growths, Shrinkages, and Deaths among Grains

The general order of procedure was as follows. The specimens were brought to the "preliminary structure," and one or more marked areas on each were photographed. The specimens were then deformed, by rolling or otherwise, and the same areas were again photographed. The specimens were then given a series of anneals, either at the same temperature or at repeatedly rising temperatures; after each anneal, each specimen was examined under the microscope, a print of the previous photomicrograph being available for comparison. If thought advisable, a fresh photomicrograph was prepared. In general, the series was continued until the changes in the marked area ceased to be important. Altogether 191 photographs were taken, while a still larger number of microscopic examinations, without photographs, were made.

It is, of course, impossible to reproduce all the photomicrographs, but Figs. 7 to 11 show the nature of the changes observed on one particular specimen UP. Fig. 7 shows the microstructure of a marked area in the preliminary state; Fig. 8 shows the same area after the whole specimen had been rolled to 24 per cent. elongation. Several of the old grains are still recognizable, although greatly distorted by the rolling; but in certain parts of the specimen, notably in the bottom and in the right-hand top corner, the old structure appears to have been replaced by seemingly new grains. Evidently, therefore, some self-annealing has occurred during or just after the rolling, at ordinary temperature. The specimen was then annealed as follows:

First anneal	5 min. at 125° C.
Second anneal	30 min. at 158° C.
Third anneal	1 hr. at 160° C.
Fourth anneal	3 hr. at 190° C.

The photograph taken after the first anneal showed a considerable further change, new grains appearing in the left-hand top corner, *i. e.* just where the original grains had survived the rolling. The changes of structure continued during the second, third, and fourth anneal; at the end of the fourth anneal, it seemed that none of the original grains

FIG. 7.—SPECIMEN UP BEFORE ROLLING. × 50.

FIG. 8.—SPECIMEN UP AFTER ROLLING. × 50.

survived, Fig. 9. In the right-hand top corner and right-hand bottom corner where new grains had appeared through self-annealing during rolling, no serious fresh change has occurred, although the fact that the specimen had now been etched six times necessarily altered somewhat the general appearance of the surface.

The specimen was then given a series of anneals at higher temperatures, namely:

Fifth anneal	3 hr. at 205° C.
Sixth anneal	2 hr. at 224° C.
Seventh anneal	8 hr. at 225° C.
Eighth anneal	6 hr. at 223° C.

After the fifth anneal, a considerable change had taken place, nearly the whole area being occupied by one grain; the structure at this stage is

somewhat ill-defined and difficult to make out, but during the seventh and eighth anneals, the position becomes clearer. The final structure of the area, attained after the eighth anneal, is shown in Fig. 10. Practically the whole of the area corresponding to that shown in Figs. 7, 8, and 9 is part of one huge grain, but the beginning of another large grain is seen on the left-hand bottom corner. Just outside the limits included in the photograph, several quite small grains still survive; it is by means of these that we can be sure that the area included in Fig. 10 is that shown in Figs. 7, 8, and 9.

FIG. 9.—SPECIMEN UP AFTER FOURTH ANNEAL. × 50.

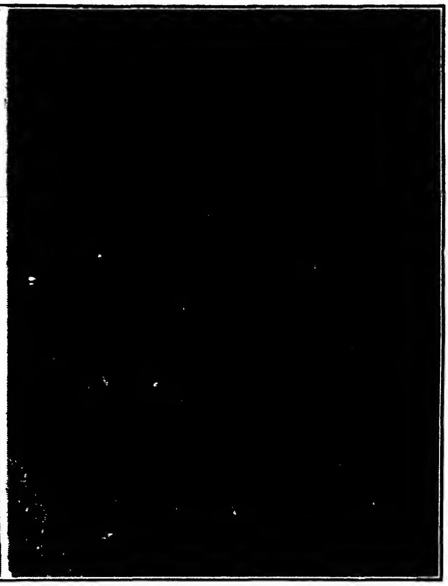
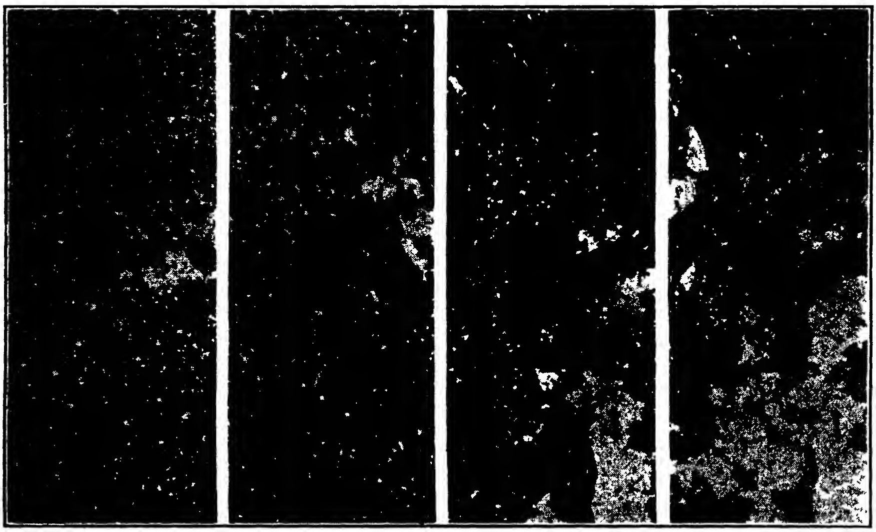


FIG. 10.—SPECIMEN UP AFTER EIGHTH ANNEAL. × 50.

The absorption of the whole area by one grain is due not to the expansion of a grain from within the area, but to invasion from outside. This is shown by approximately natural size photographs comprising nearly the whole specimen. Fig. 11 (*a*) shows the structure after the fourth anneal (the same stage as Fig. 9); already in one place some large grains have arisen, and one of them overlaps into the marked area. In (*b*) is shown the structure after the fifth anneal, the illumination being altered slightly to emphasize the newly arrived large grains. Several fresh large grains have arisen and the marked area is now mainly occupied by large grains. View (*c*), taken after the sixth anneal, shows the further formation of large crystals; more than half the whole specimen is now occupied by these huge grains. After the seventh anneal the whole specimen consists of large grains, with a few small ones embedded in them, as shown

in (*d*). The specimen was photographed after the eighth anneal, but no appreciable change had occurred.

It should be noticed that this formation of large crystals in a specimen that has already undergone complete recrystallization must involve the destruction of new (and presumably undistorted) crystals. It must probably, therefore, be distinguished from the crystal growth observed by Carpenter and Elam in antimonial tin, wherein some of what are apparently the original grains grow at the expense of others. It seems, however, to be closely analogous to the effect noticed by Carpenter and Elam[46] in aluminum, a metal in which the atoms are arrayed on the same type of space lattice as in lead. They write "recrystallization is



(*a*) (*b*) (*c*) (*d*)

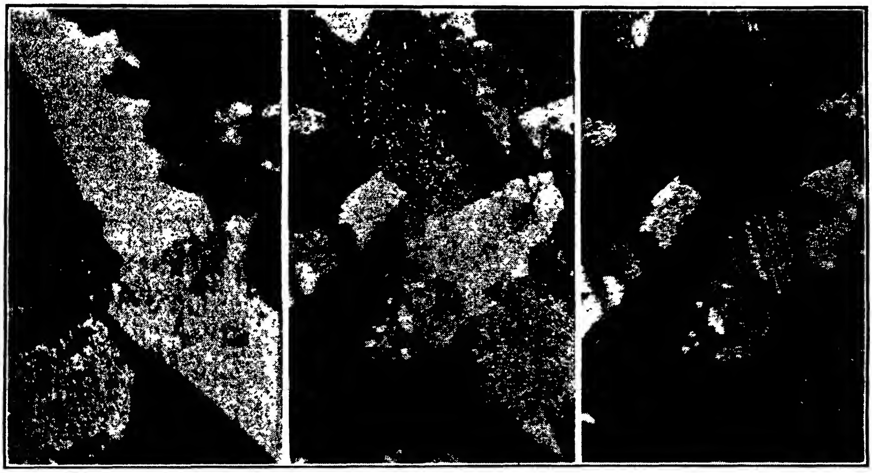
FIG. 11.—PHOTOGRAPH OF ENTIRE SPECIMEN UP: (*a*) AFTER FOURTH ANNEAL, (*b*) AFTER FIFTH ANNEAL, (*c*) AFTER SIXTH ANNEAL, (*d*) AFTER SEVENTH ANNEAL.

complete in 1 hr. at this temperature (550° C.). The crystals increase slightly in size up to 3 or 4 days. After this, a few large crystals begin to appear on the surface of the sheet. They are so far apart that many sections might be taken before including one of them. In a week, however, the sheet is largely composed of them, with small unchanged crystals between. Some of the small isolated crystals seem to persist indefinitely." We noticed this persistence of small isolated crystals within the large grains in lead also; they are clearly shown in Fig. 11 (*d*).

In the earlier stages of the changes, we were greatly helped in securing correct superimposition when comparing the photomicrographs representing different stages, by the fact that if the specimens were etched

[46] H. C. H. Carpenter and C. F. Elam: *Jnl.* Inst. Met. (1920) **24,** 123.

rather heavily before an anneal and lightly after the anneal, the photograph showed not only the new grains, but, more faintly, the boundaries of the old. If the specimen was then etched more heavily, the old boundaries disappeared entirely, the new structure being shown even more clearly than before. As an example three photographs of part of the specimen TB are shown in Fig. 12. The structure after rolling is shown in (*a*), the same area after annealing for 2 min. at 125° C., with light etching in (*b*), and in (*c*) the specimen after it was again etched for 3 min. View (*b*) is, in effect, a "composite photograph" of (*a*) and (*c*); in it, the new grains of (*c*) are clearly visible, but the old boundaries of the grains of (*a*) are also traceable in places. The reason is that the



(*a*) (*b*) (*c*)

FIG. 12.—SPECIMEN TB: (*a*) AFTER ROLLING, (*b*) AFTER ANNEAL AND LIGHT ETCHING, (*c*) AFTER 3 MIN. RE-ETCHING. × 50.

system of facets and pittings produced by the etching before annealing, were not obliterated completely either by the anneal or by the comparatively light etching that followed it. It was, however, obliterated by the exceptionally lengthy etching (3 min.) to which the specimen was afterward subjected. But for the occurrence of double boundaries, we should have had great difficulty in interpreting the photographs of the specimens that had undergone complete recrystallization.

A complete series of prints showing every specimen in each stage of the treatment at which a photograph was taken was prepared, and a careful comparison was made between the prints representing different stages. In general, the comparison was made between the first and last photographs; but where there were two successive types of transformation (*e. g.* recrystallization of the area, followed by the invasion of the whole area from outside), the pairs of prints representing the first

and last stages in each type of transformation were compared separately. Every grain in the print representing the first stage was looked for in the print representing the last stage, and was recorded as being "unchanged," or as having "grown," "shrunk," or "disappeared" altogether. Each grain, after consideration, was marked in red ink in both prints, to avoid being counted twice. Any fresh grains that appear in the final print but could not be identified with any in the first print were recorded as "new grains." The results are summarized in Table 1.

The identification or non-identification of the grains in most cases presented no great difficulty, but in some cases there was considerable doubt as to whether a certain grain in the final state was really identical with a certain grain in the first photograph, or whether it was an altogether new grain. The darkness or lightness of the grain, the general arrangements of the striations, facets, or pittings produced by etching, were useful means of identification; in cases where the change was not too great, the general shape of the grains could be taken into account.

In doubtful cases, the photographs showing the old and new grains superimposed (obtained by light etching) proved very useful. It was noticed (both by the authors and previously by Carpenter and Elam[47]) that a grain could invade one neighbor and simultaneously be invaded by another.

Apart from errors of judgment, one inevitable cause of error may come in; some of the grains recorded as "new grains" may actually be old grains that in the first state failed to reach the surface but which grew up to the surface during annealing. But if it should be argued that all cases recorded here as grain births should properly be considered as grain growths, the reply is that in many cases (owing to the small thickness of the specimens) the number of submerged grains available to sprout upwards would not be sufficient to supply the number of "apparent births" observed. Nor would it be at all easy to imagine that grain growth, so rare on the surface, should be so common in the interior. The error due to the cause mentioned is probably not great.

It occurred to the authors as just possible that the comparatively infrequent cases of "grain growth" might be illusory, being for instance cases of mistaken identity; but it is somewhat difficult to accept this view. In some instances, a grain was observed to grow only into one of its neighbors, its shape (often very characteristic) remaining unchanged on all other sides; in such cases, there is no doubt but that we are observing one and the same grain. In order to see whether the apparent growth of grains might not be due to the removal of a perceptible slice of the surface, which might cause an apparent shift in the position of the boundary in cases where the intergranular surface was not perpendicular to

[47] H. C. H. Carpenter and C. F. Elam: *Jnl.* Inst. Met. (1920) **24**, 103.

TABLE 1.—*Results of Investigation*

Specimen and Area Mark	Treatment	Identifiable Grains			Non-identifiable	
		Un-changed	Grow-ing	Shrunk	Old Grains Disap-peared	New Grain Ap-peared
UA	Squeezed three times for 2 min. each between celluloid in vise; annealed 2 min. at 100° C. then 2 min. at 175° C.	7	0	6	0	4
UB	Squeezed 2 min. in vise; annealed 2 min. at 207° C. then 10 min. at 208° C.	31	4	9	8	11
UE	Deeply indented with marking tool, and annealed 2 min. at 207° C.	25[a]	0	0	82	80
UF	Lightly indented with marking tool, and annealed (2 min.each) at 100°, 137°, 168°, 185°, 201°, and 223° C.	156	0	0	0	0
UI	Deeply indented with marking tool and annealed 3 min at 100° C. (produces no change) then 2 min at 120° C.	0	0	0	68	69
UJ$_1$	Deeply indented with marking tool, and annealed for 2 min at 110° C, 2 min at 109° C, 2 min. at 116° C.	>3 numerous small grains also unchanged	1	2	8	7
UJ$_2$	As UJ$_1$ but indent less deep.	16	0	8	7	10
UK$_3$	As UJ$_2$, but indent still less deep	3	0	8	1	7
UK$_4$	Less indented than UK$_3$ Annealed (2 min. each) at 110°, 109°, 116°, 122°, 150°, and 218° C.	30	0	3	1	2
UN$_1$	Deeply indented with marking tool and annealed at 110° for 5 min (no change produced) then at 164° C. for 5 min.	5	2	9	14	17
UN$_2$		0	0	0	42	44
UN$_3$		0	1	6	19	15
UO	Rolled to 3 5 per cent. elongation; annealed 5 min at 110° C.	0	0	1	16	16
UP, early stages	Rolled to 24 per cent. elongation; annealed 5 min. at 125° then 30 min at 158°, 1 hr. at 160°, 3 hr at 190° C.	0	0	0	51	98
UP, later stages	3 hr at 205°, 2 hr. at 224°, 8 hr. at 215°, 6 hr. at 223° C.	13	0	0	85	11
UR$_1$, early stages	Rolled to 95 per cent. elongation and given same thermal treatment as UP with omission of final anneal (6 hr. at 223° C.)	0	0	0	39	102
UR$_1$, later stages		1	0	0	101	20
UR$_2$, early stages		0	0	0	50	135
UR$_2$, later stages		27	3*	3	about 75	15
UR$_3$, early stages		0	0	0	75	129
UR$_3$, later stages		43	3	1	7	15
RQ	Area defined by pinholes, rolled until surface is just "smeared," annealed at 100° C. for successive periods of 2 min., 2 min., 2 min., and 1¼ hr.	2	1(?)	5	13	18
TB	Rolled to 10 per cent. elongation and annealed 2 min. at 125° C.	0	2	0	10	25
TC	Squeezed six times for ½ min. each between celluloid in vise, annealed (for 2 min. each) at 164°, 189°, and 211° C.	39	0	0	0	0

[a] A zone of small grains running right across the original has remained unchanged, all other original grains have disappeared.

* One grain has grown on one side but shrunk on another.

the surface of the specimen, special experiments were performed. Photographs of the same specimen were prepared after a short etching and after very prolonged etching, and compared with one another. It was found that etching continued for a time greatly exceeding that used in the main series of experiments produced no measurable movement in the grain boundaries.

A consideration of the numbers given shows that "chance" comes into the lives of grains quite as much as into the lives of men. The greater the deformation and the higher the temperature of annealing, the greater is the probability that within a given small area a change will be produced; thus as the deformation and the annealing are made more severe, the number of unchanged grains diminishes and the cases of disappearance of old grains and birth of new grains increase.

The principal new fact disclosed by the research is that the cases of the grain growth of original grains are extremely scarce; the main form of change is the formation of new grains, which grow at the expense of the old ones and, in extreme cases, cause the old ones to disappear altogether. Thus recrystallization and not grain growth is the main mode of reorganization in lead. It seemed to us that the new grains generally arose from the boundaries of the old grains, and often from places where three grains met, but we do not wish to be definite on this matter. A very important point shown by the work is that it is absolutely necessary to study the fortunes of each individual grain in the area in order to arrive at the extent of the change. In many cases, the number of new grains born in an area was approximately the same as that of the old ones that had perished; if a measurement of average grain size alone had been used as a criterion of change (as is so often done) these cases would have been recorded as showing no change.

The changes observed at temperatures below about 200° C. are well in accordance with the general view of the formation of nuclei in the disorganized material, as set forth earlier in this paper. The greater the deformation, the greater is the amount of disorganized matter, and consequently the greater is the probability of the birth of new grains; the probability increases, *ceteris paribus*, as the temperature is raised. But the formation of large grains observed by us above 200° C. in lead, and the analogous phenomenon observed by Carpenter and Elam in aluminum after recrystallization, are more difficult to explain. If we are right in thinking that this second type of change usually sets in when the original recrystallization is really complete, and when the metal consists only of new and perfect grains, free from internal stresses, one of two explanations is possible. It may be supposed that a small amount of fresh deformation is produced accidentally in handling the specimen; it must be remembered that the degree of deformation needed to cause structural changes in lead when heated above 200° C. or in aluminum when heated at 550° C.

is probably very small. This explanation, however, is not easy to accept, as accidental deformation, if sufficiently widespread to cause change throughout the whole specimen, would be likely to be intense at some places at least, and a local zone of quite small grains would be expected; this fine zone is not obtained. Yet the only alternative is to suppose that in lead above 200° C. (and presumably in aluminum at 550° C. also) stress is not needed to produce grain growth; this conclusion would be of interest, in view of the fact[48] that cast cadmium undergoes structural changes at high temperatures, without the application of mechanical stress.

It would appear therefore convenient to distinguish two types of change in lead: (1) Changes noticed at low temperatures, which are comparatively rapid, often becoming complete within a few minutes, and which depend on the previous deformation of the material; these are best explained as cases of reorganization of the disorganized material: (2) changes noticed at higher temperatures (above 200° C.) leading to the spreading of a few large crystals over the whole specimen; they usually take several hours to complete. These changes seem probably not to be the direct result of the original mechanical deformation.

Our main observations confirm the observations of Ewing and Rosenhain[49] on annealing changes in lead; the differences met with may be ascribed to the fact that our method of working, chosen specially to give results capable of yielding statistical evidence, was somewhat different from that adopted by those experimenters.

Influence of Degree of Deformation and Annealing Temperature on Structure

A study of Table 1 enables us to conclude that lead conforms to the generally accepted principles of recrystallization in two important respects. First, the greater the deformation, the greater is the change produced; the proportion of grain births, grain deaths, and grain shrinkages increases with the deformation, while the proportion of unchanged grains decreases. Second, the temperature required to produce a change sinks as the deformation increases; if the deformation is sufficient, recrystallization may occur at ordinary temperatures.

However, to obtain rather more precise information regarding the self-annealing qualities of lead, a special series of experiments was performed, in which strips of lead were rolled to different elongations, a marked area being photographed before and after the rolling; the photographs were then compared and the number of grains recognizable in both were counted. As pronounced rolling necessarily shortens the

[48] M. Cook: *Trans.* Faraday Soc. (1923) **19**, 43.

[49] J. A. Ewing and W. Rosenhain: *Phil. Trans.* [A] (1900) **195**, 284.

dimensions of the grains in one direction, and lengthens them in another, it was not possible to classify the identifiable grains further as being unchanged, growing, or shrunk. The results are shown in Table 2.

TABLE 2.—*Results of Self-annealing of Lead*

Specimen Mark	Percentage Elongation	Old Grains Recognizable	Old Grains Disappeared	New Grains Appeared
XA	5	158	0	0
XB	10	53	1	3
XC	20	18	21	30
XE	30	5 (greatly distorted)	136	115
XF	40	about 5 (recognition doubtful owing to great distortion)	127	164
XG	50	0	50	130
XH	64	0	79	122

The results show that in the specimen subjected to only 5 per cent. elongation, all the grains in the area can be recognized afterwards; but that with deformations of 30 per cent. or over, nearly complete recrystallization occurs at ordinary temperatures. Thus lead is not in any absolute sense a self-annealing metal; it only undergoes self-annealing if deformed sufficiently. This explains a phenomenon that has been noticed in lead during the present research, and had previously been observed by one of the authors in cadmium. The first effect of rolling is perceptibly to harden the metal, as indeed is the case with most metals; but after a certain point the metal becomes soft again. Undoubtedly this is because metal at that point has become sufficiently deformed for self-annealing to set in at ordinary temperature.

It should, of course, be noticed that it is wrong to speak of a "critical deformation" just sufficient to produce recrystallization at room temperatures. As we increase the deformation gradually from 5 to 30 per cent., the proportion of old grains that survive the treatment gradually falls from 98 to 3 per cent.

The work of Norbury,[50] published after the completion of our experiments, is in close agreement with our work as regards the value of the deformation needed to produce spontaneous annealing in lead, although a different method was used. Norbury measured the Brinell hardness of specimens of hammered lead at various times after the completion of hammering; he found that lead reduced by 10 per cent. lost its work hardness only very slowly and very partially. Where the reduction had been 15 per cent., a greater fraction of the work hardness was lost, but the

[50] A. L. Norbury: *Trans.* Faraday Soc. (1923) **19**, 140.

loss was comparatively slow. Lead hammered to 30 per cent. reduction lost its acquired hardness quite rapidly and very completely.

It seemed profitable to make a study of the annealing temperature of tin, another metal which is often loosely described as possessing self-annealing properties. Specimens of tin with certain areas photographed, were rolled to various elongations (4, 8, 15, 28, 53, and 110 per cent.), kept for 8 days at ordinary temperatures, and again examined. They were then subjected to the following annealing operations in turn, being examined and, if considered necessary, photographed, after each anneal; the first four anneals were carried out by immersion in heated aniline.

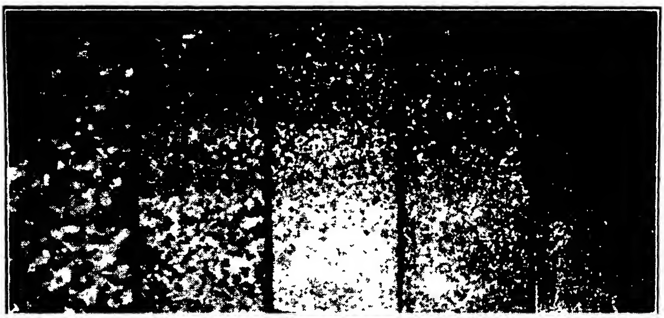
First anneal	35 min. at 40– 45° C.
Second anneal	30 min. at 71– 76° C.
Third anneal	30 min. at 100° C.
Fourth anneal	40 min. at 160° C.
Fifth anneal	15 min. at 210–220° C.

The structure of the rolled tin was extremely hazy, and rendered statistical study quite impossible. In the specimen with 15 per cent. elongation, the structure was so poor that, after the first anneal, it was not considered worth while to proceed with this specimen. Apart from this fact, rolling necessarily deforms the grains, which become perceptibly elongated in one direction, and this would in any case render identification difficult. However, it was possible to ascertain that in the specimens, which had received 4, 8, and 28 per cent. elongation, nearly all the more conspicuous grains present before the rolling were present after the rolling. Apart from the distortion referred to, there is no certain indication that any change of structure had occurred at ordinary temperature. In the case of the specimen rolled to 53 per cent. elongation, only 5 out of 64 original grains could be recognized after rolling; but this may have been due, at least in part, to the general disorganization of the whole area; in the specimen elongated to 110 per cent., none of the original grains could be recognized. Whether this was due to self-annealing or not, it has been made clear that tin does not undergo serious self-annealing at ordinary temperature, if the deformation has been only moderate.

Even the first two anneals (at 42° and 73° C.) produced no serious changes of structure. The specimens rolled to 28 and 53 per cent. elongation, however, showed a marked change of structure on annealing at 100° C., while those elongated 4 and 8 per cent., respectively, showed no change until the fourth anneal at 160° C. The change of structure, when it did take place, was very marked; the haziness disappeared and new (or apparently new) grains much larger than the original grains, and fairly well defined, appeared. In the case of the specimen with 4 per cent. elongation, the change of structure was very striking, and was visible to the naked eye. When this specimen was etched after the

fourth anneal, the ill-defined structure, due to a fine debris of grains, was observed to clear away, and a clean well-defined series of large, glistening grains appeared. Photomicrographs at this stage showed the boundaries both of the old and the new grains, as in lead, but, after the fifth anneal and further etching, the double boundaries had disappeared and the new grains (the boundaries of which had scarcely altered) alone were seen. After the last anneal, the specimens were placed side by side and photographed (Fig. 13). The grain size varies with the deformation according to the usual rule, being greatest in the least deformed specimen.

A series of experiments was then carried out with cadmium, with a view to ascertaining the effect of varying the degree of deformation and the annealing temperature on the grain size. It appeared important that the specimens should be brought rapidly to the requisite temperature



4 8 28 53 110
Per Cent. Deformation

FIG. 13.—TIN SPECIMENS AFTER PROGRESSIVE ANNEALING. × 0.6.

and the oil-bath method was found to be suitable. Six degrees of deformation (5, 10, 15, 20, 35, and 50 per cent.) and five temperatures (55°, 75°, 101°, 137° and 174° C.) were employed. Photomicrographs were prepared of representative areas on all the 30 specimens and, after examination, the prints were pasted upon cardboard, and the series again photographed, so as to reproduce the whole on a reduced scale, Fig. 14.

The results show clearly that at low annealing temperatures, the grain size decreases as the degree of deformation increases. This is explained on the supposition that recrystallization occurs in the disorganized material, the amount of which increases with the deformation; evidently at low temperatures, deformation is necessary for structural change on annealing. But they show also that at higher annealing temperatures, the grain size attained depends very little on the deformation, which again seems to afford support for the view already suggested, that the production of coarse grains which occurs at comparatively high temperatures is a process independent of the existence of stresses or deformity in the crystals.

After all, there is nothing remarkable in the supposition that deformation is necessary for structural changes at low temperatures but not at high temperatures. Undoubtedly the only entirely stable condition of a piece of metal will be a state in which the whole specimen is one crystal; in a polycrystalline specimen the change of alignment of atoms at the boundaries of the crystals must represent a departure from the condition of maximum stability. A small decrease of energy (namely the interfacial energy originally resident at the intergranular boundaries) will occur where a polycrystalline specimen undergoes change to a monocrystalline specimen, although this decrease of energy will be far

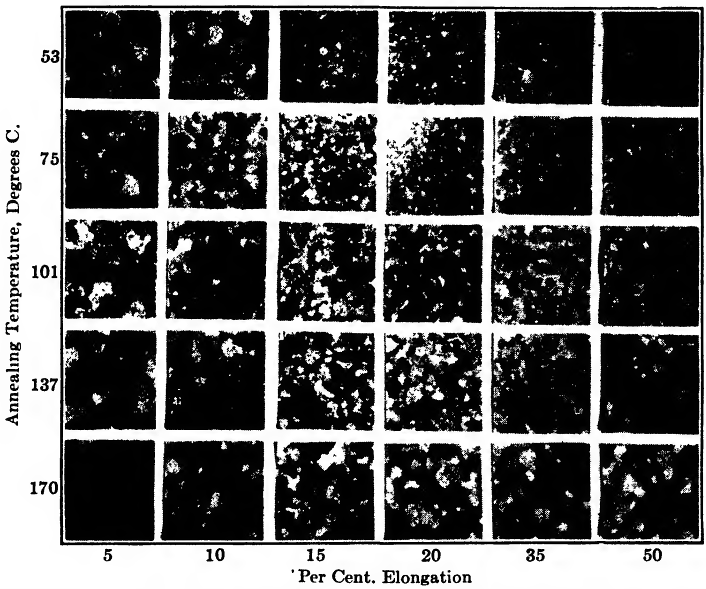


FIG. 14.—GRAIN SIZE OF CADMIUM DEFORMED AND ANNEALED UNDER DIFFERENT CONDITIONS. × 8.

smaller than would occur if a deformed or shattered crystalline specimen were to pass to the perfectly orientated crystalline condition. It is quite to be expected that the change involving the large decrease of energy may occur at quite a low temperature, the temperature being lowest when the shattering or deformation is most severe, but the change involving only a small decrease of energy (*i. e.*, the change of an undeformed polycrystalline specimen to the monocrystalline state) will only occur at higher temperatures not very far below the melting point, that is to say, temperatures at which the atoms begin to have oscillations of considerable amplitude.

The results of the work on cadmium give no indication of the existence of the alleged allotropic change about 60° C.

Acknowledgments

The experiments were carried out in the Goldsmiths' Laboratory of Metallurgy, Cambridge University by permission of Mr. C. T. Heycock, F. R. S.; we wish to express our thanks to Mr. Heycock for help and advice throughout the investigations. We are also indebted to Mr. F. T. Stoakley for loan of photographic apparatus.

DISCUSSION

M. F. Fogler,* Chicago, Ill. (written discussion).—The authors have apparently overlooked a paper by R. S. Dean and W. E. Hudson,[51] which attempts to cover the grain growth of a soft metal from a quantitative-statistical standpoint. The work of these investigators indicates that a more satisfactory analysis of the effect of increased temperature on grain growth in a uniformly deformed specimen may be arrived at than that given in the paper under discussion. They show that an increase in temperature does not greatly affect the velocity constant of grain growth, if that velocity is capable of expression by the equation of a monomolecular reaction. The apparent increase in velocity of grain growth with temperature is, according to their views, due almost entirely to the effect of temperature on the ultimate or equilibrium grain volume. This grain volume is an exponential function of the temperature and may be expressed by an equation of the form $V = Be^{\frac{-A}{T}}$ where B and A are constants and T the absolute temperature. The exponential form is arrived at by assuming a maxwellian distribution of energy among the atoms that have been affected by the deformation and considering that only those with more than a certain critical energy will undergo grain growth. Their experimental work on lead-antimony alloy seems to justify this method of analysis of grain-growth phenomena and further work done in the Western Electric laboratories on similar alloys is in accord with this mode of analysis.

* Metallurgical Engineer, Western Electric Co.

[51] *Jnl.* Amer. Chem. Soc. (August, 1924).

Eutectic Patterns in Metallic Alloys

By C. H. Green,* Minneapolis, Minn.

(New York Meeting, February, 1925)

Recently two papers on the structure of eutectics were read before the British Institute of Metals, one by F. L. Brady[1] and the other by A. Portevin.[2] In the preparation of photomicrographs of laboratory specimens as illustrations for student work, and in connection with various researches, the writer has been working along the same line for some time and, therefore, was much interested in the results given, especially those of Portevin. He has correlated the information on the subject and has outlined a broad scientific basis for future work along this line. It is largely with the idea of adding something by way of illustration to the work already done that this paper is written.

The eutectic is generally understood to mean the alloy having the lowest melting point of any alloy of the system, and in which the melt becomes supersaturated with reference to the two or more phases which separate out simultaneously or alternately. From the surface pattern, the eutectic means a structure with no primary crystals. It is not always easy to get the exact eutectic composition in making any alloy; in fact, a slight range in composition may be expected and some of the coarser particles may be richer in either of the composing metals. Even when chemical analysis shows the right composition, differences in density of the pure metals may cause segregation, or supercooling resulting from different crystallizing properties may give a surface pattern the appearance of being on one side of the eutectic point. However, the alloys on either side of the eutectic composition, showing primary crystals of one of the phases and the effect of the proeutectic form on the surface pattern of the eutectic make a very interesting study, which is slightly touched upon in this paper.

The phases, or microconstituents, of a eutectic may be pure metals (Pb-Sb, Tl-Au), solid solutions (Cd-Zn), a pure metal and a solid solution (Ag-Sn), or a pure metal or solid solution with an intermetallic compound (Sb-Mg, Sb-Cu, As-Cu, Bi-Te, etc.).

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[1] *Jnl.* Inst. Metals (1922) **28**, 369.

[2] *Jnl.* Inst. Metals (1923) **29**, 239; *Engineering* (1923), **115**, 447, 477, 505.

Preparation of Specimens

Melts were made up in the metallographic laboratory of the School of Mines with the usual precautions. All specimens were cooled sufficiently slowly to have an annealing effect. No effects of long annealing or of chill casting have been taken into account. The compositions given are the intended compositions and not the results of chemical analyses. Unless otherwise stated the values are in weight per cent. No attempt has been made to work out constitution diagrams or to find the exact composition of the eutectics, but diagrams given in the literature have been taken as an indication of the constituents present when confirmed by microscopic examination.

Magnifications and Etching Reagents

As fineness of grain or of eutectic colony depends on rate of cooling, velocity of crystallization, etc., any magnification has been used that will clearly show the pattern, usually $\times$ 75, $\times$ 100, $\times$ 150, or $\times$ 200. Usually, several etching reagents were tried on the specimens but only the one finally used to bring out the structure is listed with the photomicrograph.

Classification

From the standpoint of "morphology" of the eutectic, by which is understood the form or shape and relative distribution of the particles or elements, Portevin gives the following classification:

Type I. Regular crystals.

Type II. Dendrites or skeleton crystals: (*a*) Regular dendrites; (*b*) irregular or badly formed dendrites; (*c*) skeleton crystals or partly formed crystals.

Type III. Arrangement in eutectic colonies or complex grains.

1. A diverging or radiating variety in which the particles thicken out toward the ends. Spherical. These particles in the colonies may be: (*a*) Rounded, dotted, or spheroidal; (*b*) flattened, or in more or less wavy sheets; (*c*) branching, producing a dendritic appearance in the peripheral zones.

2. The fanlike variety, with slightly divergent particles contained within a narrow cone. Conical.

3. Parallel-clustered variety, occurring as minute rods grouped together in parallel arrangement.

Type IV. Granular. Not found in metallic eutectics and later disregarded.

Obviously, other types may be discovered in the study of eutectics; the boundaries between these types are not clearly marked as yet and there seem to be transition forms. Apparently, however, every eutectic conforms to some ideal type, determined largely by the properties of the

pure metals making up the system, and when we have finally taken into account all the influencing factors and have found the true type of any eutectic, that type is fixed and, though there may be slight temperature and concentration variations during solidification which affect the relative amount of each constituent deposited and the size of the colonies in different parts of the specimen, these variations will be subservient to the typical development of any system and will easily be recognized as such. Further study should also show the effect of chill casting or of long annealing on the pattern in any particular type.

Type I. Regular Crystals

It is not my intention to discuss every type and variety mentioned, but to add a few illustrations of the types given and to suggest some slight changes in the classification. No illustration of Type I is given.

Type II. Dendrites or Skeleton Crystals

Lead-bismuth and bismuth-tin are given as examples of Type II. Lead and bismuth (Figs. 1 and 2) form two solid solutions, α a solution bismuth in lead up to some 20 or 30 per cent. and β a solution of lead in bismuth to approximately 1 per cent. In the photomicrograph, the light constituent β is almost pure bismuth. Two fields are shown, both found in one specimen and both typical, but Fig. 2 shows the formation cut at a different angle. In the bismuth-tin alloy (Figs. 3 and 4) the light colored areas are practically pure bismuth which forms skeletons around which the tin-rich solid solution is disposed. The surface patterns of bismuth-lead and bismuth-tin eutectics are very similar, both showing the same angularity of design and both showing the predominating influence of the bismuth. Brady[3] puts these in the angular class but admits that these eutectics may almost be called "dendritic" type; Desch[4] says they are characterized by boxed forms or simple polyhedral crystallites divided transversely by parallel bands; Portevin[5] calls them a transition form between Types I and II, showing some regular dendrites and some areas "regularly formed in such a manner that the shell or layer reproduces a cubic or pseudo-cubic crystal." It appears to the writer that Type II should cover angular forms, dendrites whether regular or irregular, skeleton forms, and any like formation.

Type. III. Eutectic Colonies

The term "spherulitic" is most applicable to this type of structure even though few perfect spheres are found. The "madreporic" structure of Portevin, named from the resemblance to the growth of a coral polyp

[3] *Loc. cit.* [4] "*Metallography*," 186. [5] *Loc. cit.*

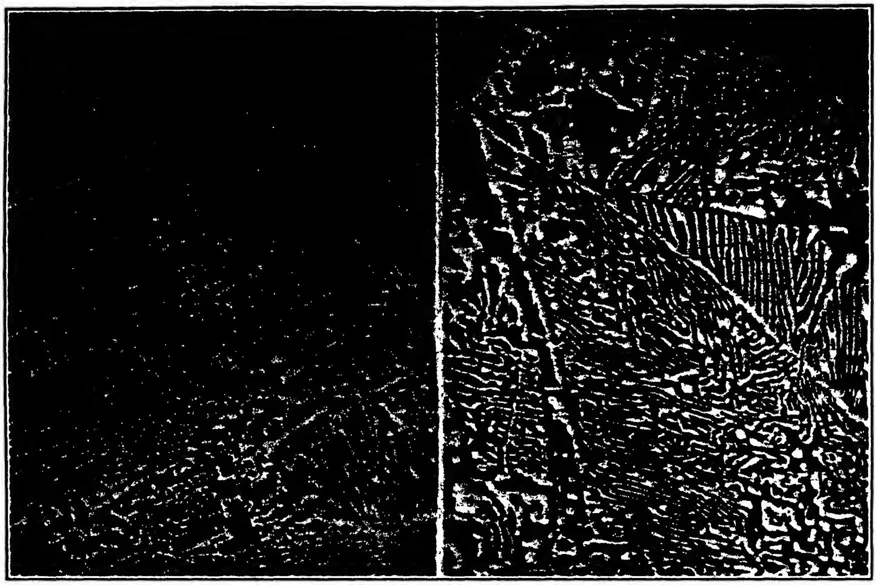

Fig. 1. Fig. 2.

Figs. 1 and 2.—Alloy containing 57 per cent. bismuth and 43 per cent. lead. × 100. Etched with conc. HNO_3.

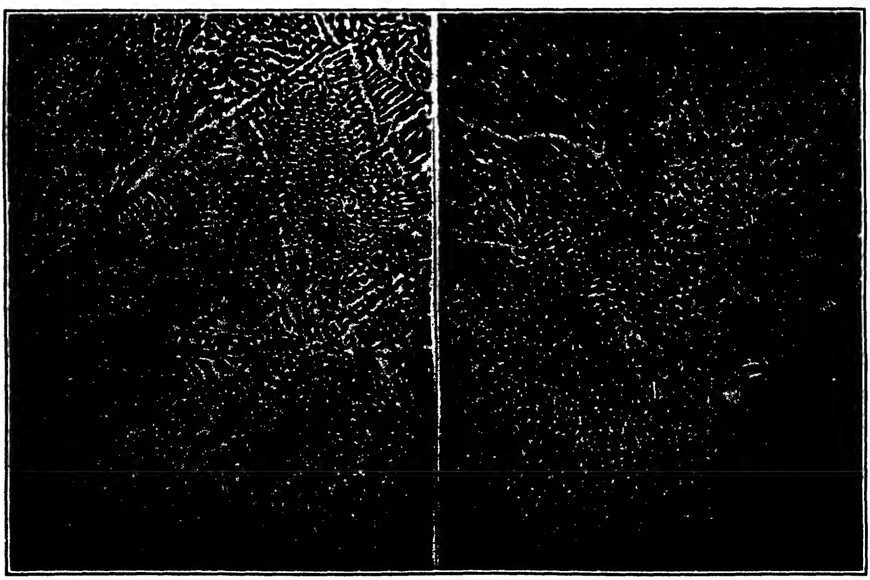

Fig. 3. Fig. 4.

Figs. 3 and 4.—Alloy containing 58 per cent. bismuth and 42 per cent. tin. × 100. Etched with conc. HCl.

and illustrated by a branching treelike growth from the outside of the crucible charge to the center is, in some cases at least, the result of chill casting. Brady[6] uses the same form of illustration to show the rodlike growth of a eutectic and quenched his alloys. He says "by quenching molten eutectic alloys similar structures can be obtained in many other cases, and this rodlike (stäbchen) structure has been produced in lead-tin, zinc-tin, and copper-silver eutectics . . ." It has also been observed in this laboratory that such structures could be produced by chill casting,

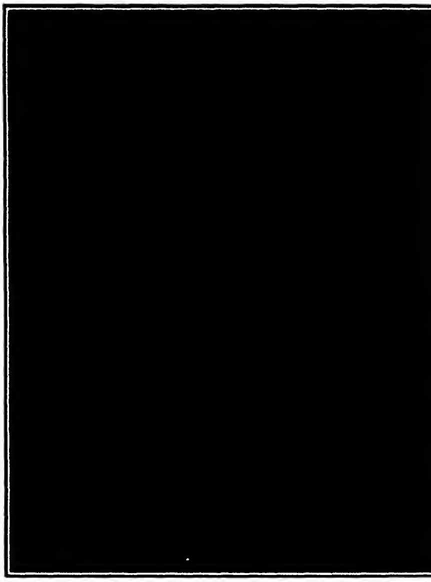

FIG. 5.—ALLOY CONTAINING 30 PER CENT. CADMIUM AND 70 PER CENT. TIN. × 100.

FIG. 6.—ALLOY CONTAINING 82 PER CENT. CADMIUM AND 18 PER CENT ZINC. × 100.

ETCHED WITH 10 PER CENT. HNO_3.

for example in cadmium-zinc alloys. Furthermore, a similar growth has been found in eutectics that do not show typical eutectic colonies in the microstructure. However, Type III has certain distinguishing characteristics—complex grains or crystalline colonies having the interior of a finer structure than the outer layers which are enlarged and coarsened.

It seems that one variety, the spherical, should cover Type III, as it is the spherulitic type. The differences in the patterns come from the different forms or arrangements of the particles within the colony. Cadmium-tin, cadmium-zinc, tellurium-tin, and white cast iron furnish good examples of this type.

[6] *Loc. cit.*

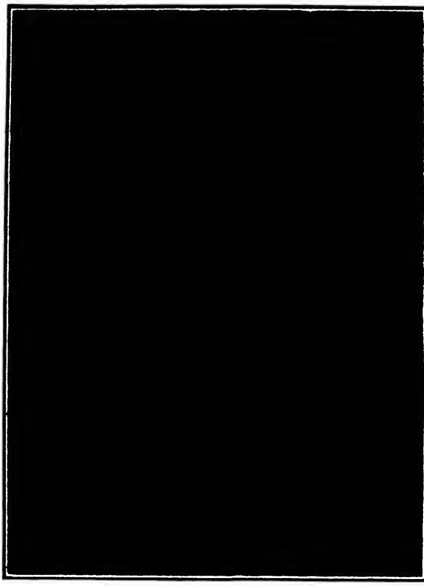

Fig. 7.—Alloy containing 86 per cent. tellurium and 14 per cent. tin. × 100.

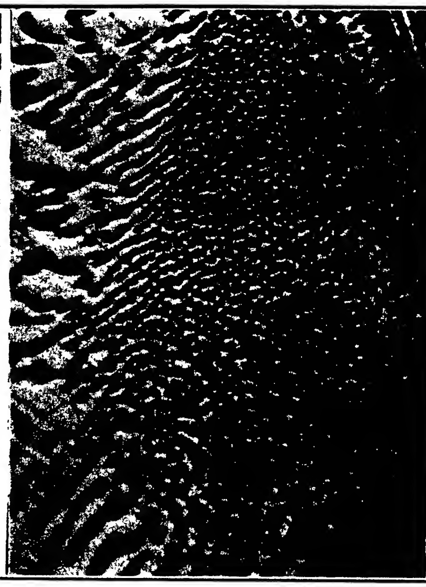

Fig. 8.—Same alloy as in Fig. 7. × 1000.

Etched with 10 per cent. HNO_3.

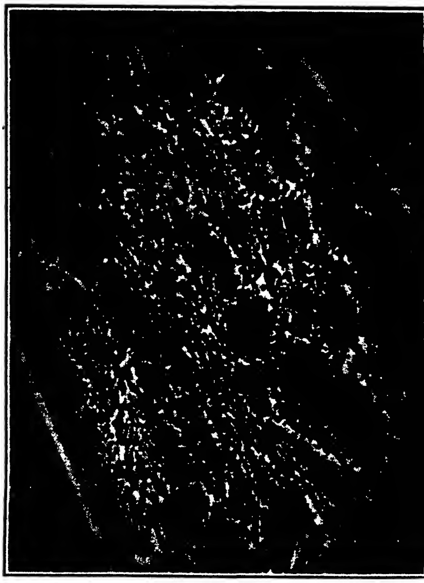

Fig. 9.—White cast iron. × 50.

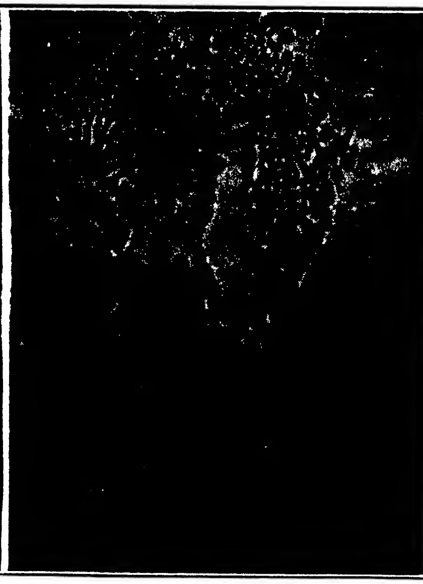

Fig. 10.—White cast iron. × 500.

Etched with picric acid.

The miscibility of tin and cadmium is low. Schleicher[7] says cadmium dissolves practically no tin in the solid phase, so the light constituent in the photomicrograph (Fig. 5) is practically pure cadmium with here and there an area of primary cadmium crystals separated out because of the supercooling of the tin. The colonies are clearly shown with fine parallel or wavy lines in the center and a thickening of the outer portions giving in many places a fanlike border.

The cadmium-zinc eutectic is the most common illustration of this form (Fig. 6). The pattern is practically the same as the cadmium-tin.

Fig. 11.—Alloy containing 20 per cent. lead and 80 per cent. tellurium. × 100. Etched with 50 per cent. HNO_3.

Fig. 12.—Alloy containing 39 per cent. tin and 61 per cent. magnesium. × 100. Etched with 1 per cent. HCl in water.

The mutual solubility is so low that the light constituent in the photomicrograph is nearly pure cadmium and the dark nearly pure zinc, which is attacked by the etching reagent. In some of the colonies, the centers have a dotted appearance, depending on the direction of the plane of observation to the orientation of the crystal.

The eutectic of tellurium with the compound TeSn forms one of the most striking and beautiful structures of this class examined, see Figs. 7 and 8. Whole series of eutectic colonies are plainly visible with a variety of parallel bands, wavy plates, and fan formations. The light ground mass is tellurium.

White cast iron, the Fe-Fe_3C eutectic, is too well known to need discussion; Fig. 9 shows the arrangement in eutectic colonies. It also shows

[7] *Int. Jnl. Metallog.*, **2**, 76.

the rodlike arrangement that has led to calling this a "cylindrical" variety of Type III. The appearance of the finer particles of the colonies is brought out more clearly in Fig. 10.

Two other systems, lead-tellurium and magnesium-tin, have been studied to some extent; these eutectics show some characteristics of both Type II and Type III. Lead and tellurium form a compound PbTe that is darkened by the etching reagent; see Fig. 11. This compound cuts through the gray tellurium ground mass in angular formation and often forms dendrites, yet there seems to be a general arrangement in colonies.

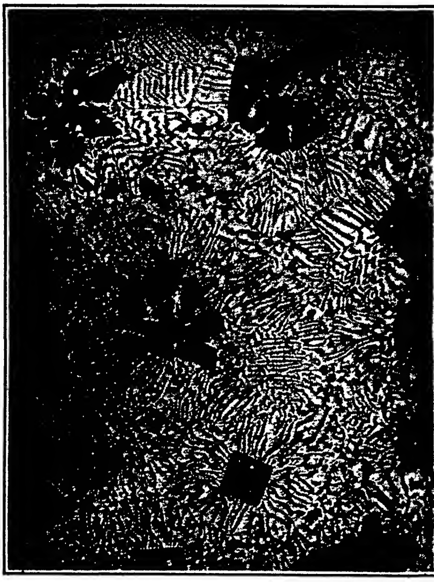

Fig. 13.—Approximately 52 per cent. magnesium and 48 per cent. tin. × 75. Relief polish and oxidized.

Fig. 14.—Approximately 82 per cent. cadmium and 18 per cent. zinc. × 100. Etched with conc. HNO_3.

Magnesium and tin form two eutectics and one intermetallic compound Mg_2Sn. Earlier writers could find no solid solution but Guertler's diagram shows a solubility of tin in magnesium up to about 9 per cent. The compound is hard and brittle and shows a crystalline fracture. Fig. 12, the eutectic Mg-Mg_2Sn, shows the colony arrangement that seems to be typical, but the particles within the colony tend to form angles. These alloys oxidize very easily but by photographing immediately after etching the compound remained white and only the solid solution darkened.

In eutectic alloys where one phase separates out first and there is local crystallization of one constituent, and in near-eutectic alloys, either hypo- or hyper-eutectic, the variation from the eutectic pattern is the same in all alloys of a given type. For example, lead-bismuth eutectic

(Type II) may show excess α (Pb) in some fields and excess β (Bi) in other fields, but the eutectic areas surrounding and adjoining these primary crystals are always angular; see Fig. 2. The bismuth-tin eutectic alloy may show dendrites of excess tin or wider bands or crystals of bismuth but they seem to have no effect on the eutectic pattern; see Figs. 3 and 4. Magnesium-tin, placed under Type III and showing a colony arrangement of the eutectic with angular centers (Fig. 12), retains its angularity if there is excess of the compound and the eutectic radiates from the crystals of Mg_2Sn. This is shown in Fig. 13 in which the compound was darkened by relief polish and oxidation.

In the alloys already given in Type III, it is interesting to watch the variation from the pure eutectic form. A general fanlike arrangement is always preserved, that is a part of a colony, but the distribution of these

FIG. 15.—ALLOY CONTAINING 90 PER CENT. CADMIUM AND 10 PER CENT. ZINC. × 200. ETCHED WITH CONC. HNO_3.

fans depends on the form taken by the excess phase. In the cadmium-zinc alloy, excess zinc may form dendrites from and around which the eutectic fans radiate; Fig. 14. If the cadmium is in slight excess, it is taken care of in the coarse boundaries of the colonies; but if in greater excess, as we go to the cadmium side of the diagram, the excess cadmium separates out as primary crystals and the eutectic arranges itself in fans around and between the crystals; see Fig. 15. Cadmium-tin shows the same tendency to separate out free cadmium crystals and the eutectic as tenaciously keeps its radiating form, a fact that applies also to lead-tin and arsenic-tin systems, though in the latter case the excess is the compound AsSn; see Figs. 16, 17, 18. An aluminum-zinc alloy of approximately 9 per cent. aluminum and 91 per cent. zinc shows the eutectic fans of the zinc-rich phase between the β crystals (Fig. 19) and indicates

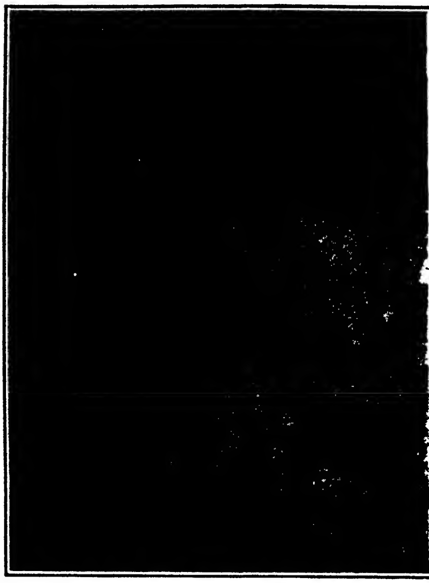

Fig. 16.—Approximately 30 per cent. cadmium and 70 per cent. tin. × 150.

Fig. 17.—Approximately 80 per cent. tin and 20 per cent. lead. × 100.

Etched with 10 per cent. HNO_3.

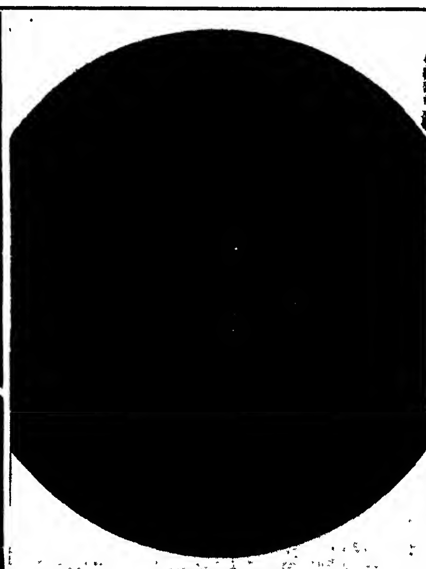

Fig. 18.—Approximately 44 per cent. arsenic and 56 per cent. tin. × 200. Etched with conc. HCl.

Fig. 19.—Approximately 9 per cent. aluminum and 91 per cent. zinc. × 100. Etched with conc. HNO_3.

that the aluminum-zinc eutectic belongs to the spherical form, a fact that has been observed.

On the other hand, where the excess phase takes a needle or platelike form, as in white cast iron or arsenic-nickel alloys, the needles of Fe_3C and plates of α solid solution of arsenic in nickel break up and displace the eutectic colonies but act as bases from which the eutectic fans extend; see Figs. 20 and 21.

When studying different systems, it was found that there is a wonderful similarity of form in the antimony-tellurium, bismuth-tellurium, and tin-zinc eutectics. Brady noted that the tin-zinc eutectic failed to follow the law of surface tension. Portevin has placed the tin-zinc eutectic in

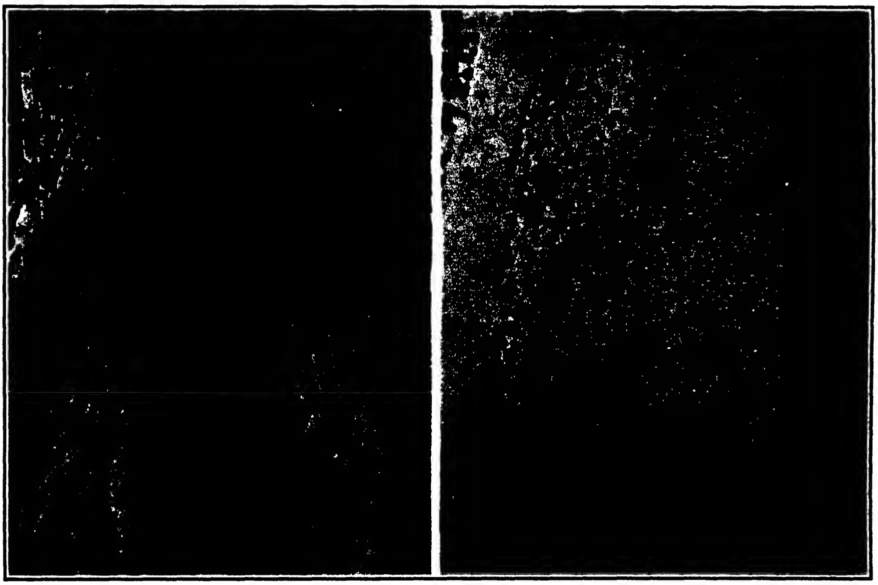

FIG. 20.—WHITE CAST IRON. × 100. ETCHED WITH PICRIC ACID.

FIG. 21.—APPROXIMATELY 20 PER CENT. ARSENIC AND 80 PER CENT. NICKEL. × 150. ETCHED WITH 10 PER CENT. HCl IN ALCOHOL.

Type III, class 2, "a fan-like variety with slightly divergent particles contained within a narrow cone." That expression describes all three of these eutectics (see Figs. 24, 26, 27) but they do not have the appearance of eutectic colonies and it is suggested that they may be considered as a separate type—a conical arrangement of one phase in a ground mass of the other phase. The microstructure seems to be characterized by straight center lines or paths through the specimen from which the cones diverge, and by scattered cones.

In the tin-zinc eutectic, the phases are the solid solution of zinc in tin and pure zinc, the latter forming the dark needles in the photomicro-

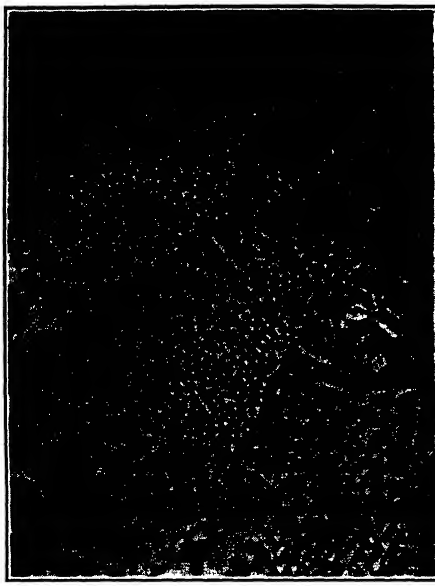

Fig. 22.—Alloy containing 77 per cent. antimony and 23 per cent. copper. × 200.

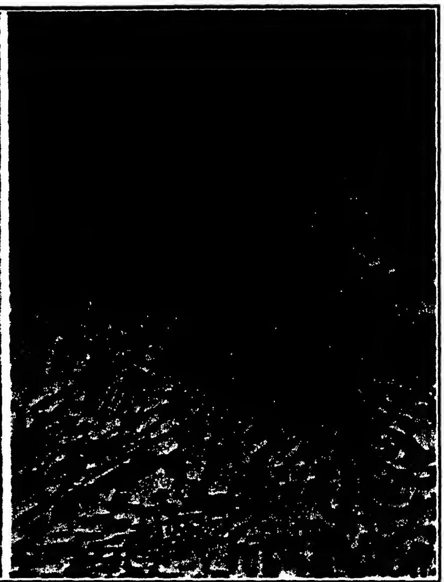

Fig. 23.—Alloy containing 77 per cent. antimony and 23 per cent. copper. × 150.

Etched with aqua regia.

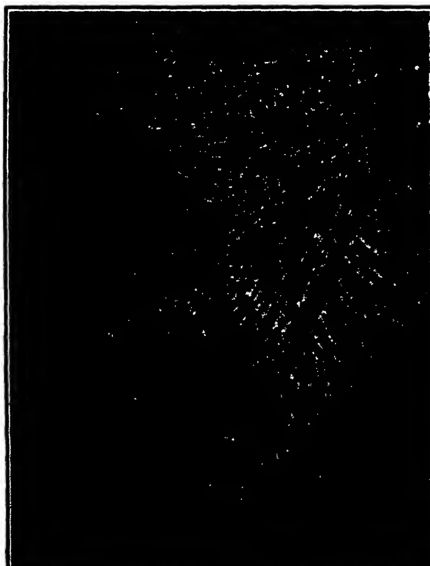

Fig. 24.—Alloy containing 91.5 per cent. tin and 8.5 per cent. zinc. × 100.

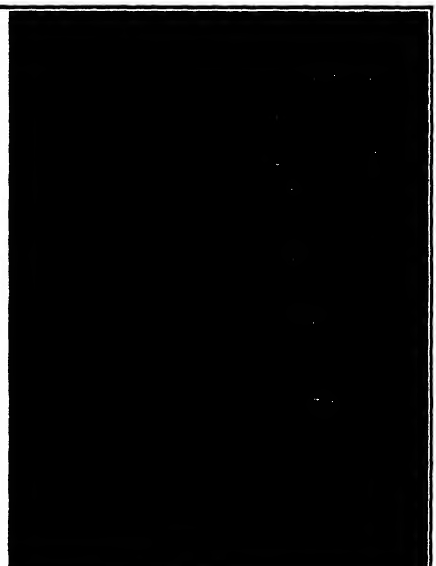

Fig. 25.—Approximately 91.5 per cent. tin and 8.5 per cent. zinc. × 100.

Etched with 10 per cent. HNO_3.

graph. When there is considerable excess of the solid solution, instead of forming dendrites with the eutectic fans between the crystals it forms a ground mass within which the needles of the zinc phase spread out in cone formation. Fig. 25 shows the grain boundaries in the solid solution and the zinc cones.

The alloy with 10 per cent. antimony and 90 per cent. tellurium forms a eutectic between Sb_2Te_3 and Te. These alloys oxidize readily but the tellurium ground mass darkens first and leaves the white needles of the compound standing out in contrast and forming the pattern. Electrolytic etching of this specimen gives the same effect.

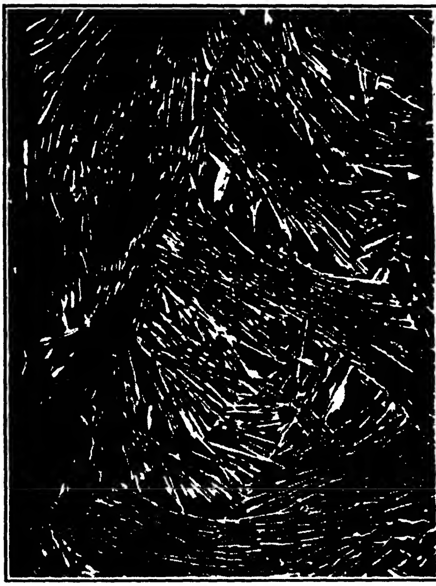

FIG. 26.—ALLOY CONTAINING 10 PER CENT. ANTIMONY AND 90 PER CENT. TELLURIUM. × 100.

FIG. 27.—ALLOY CONTAINING 12 PER CENT. BISMUTH AND 88 PER CENT. TELLURIUM. × 100.

ETCHED WITH CONC. HNO_3.

The eutectic of tellurium with Bi_2Te_3 is very similar. The gray tellurium ground mass remains unaffected by the etching reagent while the needles of compound are darkened and form the cones. With excess tellurium, the cones become scattered and present much the appearance of tin-zinc in Fig. 25.

The antimony-copper, Sb-Cu_2Sb, eutectic has been the subject of much discussion. Work on the system by Carpenter, Reimann, Braesco, Kurnakow, and others indicates that there are two eutectics and two compounds in the series and that the miscibility of antimony in copper may be as much as 8 per cent., by weight, and of copper in antimony not more than 0.5 per cent., by weight. At 77 per cent. antimony-

23 per cent. copper, the eutectic is a mixture of Cu_2Sb and of solid solution of copper in antimony or practically pure antimony. Carpenter[8] made a rather complete investigation of the Cu-Sb system and states that the eutectic showed a remarkable lack of orientation, but his specimen was annealed for six weeks. Brady says it seems to be in the crystalline class, and shows the triangular crystals of antimony. Desch gives a like illustration but also shows long plates of antimony. Portevin places it in Type III "with slightly divergent particles contained within a narrow cone."

It appears that copper tends to form eutectic colonies (Cu-Ag, Cu-Cu_2O, Cu-Cu_3P, etc.), but antimony has a strong tendency toward the angular arrangement. Antimony and Cu_2Sb are both strongly crystalline; hence the eutectic form represents a constant struggle between the two phases. Fig. 22 shows eutectic colonies in which the central particles are triangular antimony crystals. Some colonies were found with banded centers, and many areas showed a strong resemblance to the tin-zinc eutectic, see Fig. 23. Morphologically, then, the Sb-Cu_2Sb eutectic might be placed in any one of the types given; probably Type III predominates, but further study is needed to decide definitely.

Summary

After a careful consideration of the literature on eutectics, especially of the two most important recent papers, it appears that there is no disagreement in the results. The morphological classification is far more comprehensive but consideration of surface tension gives added weight to certain groups. In the few instances noted, where it seems the form does not correspond to surface tension values, some other property is probably in control. Portevin's Type I, regular crystals, easily covers Brady's crystalline class and is not often found. Every example of Brady's globular and lamellar classes forms eutectic colonies and differs in different parts of the same specimen as to whether the central particles of the colony are globular or appear lamellar. Type II, dendrites, covers all of Brady's 3A class and probably his 3B class. The following classification is suggested:

Type I. Regular crystals.

Type II. Dendrites or skeleton crystals. Angular arrangement. (One metal has a low surface tension or high cohesion. One constituent retains its own crystal form, and acts as the predominant partner. Successive crystallization.) Examples, Bi-Pb, Bi-Sn, Pb-Te, etc.

Type III. Eutectic colonies or complex grains. Spherical or spherulitic. (Metals of high or medium surface tension. Simultaneous crystallization.) Central particles rounded, dotted, parallel straight or wavy sheets, rods; possibly angular or triangular.

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[8] *Int. Jnl. Metallog.* (1913), **4**, 300.

Examples, Cd-Sn, Cd-Zn, Te-Sn, Mg-Sn, Pb-Sn, As-Sn, Al-Zn, etc.

Type IV. Conical arrangement of one phase in a ground mass of the other.

Examples, Sn-Zn, Sb-Te, Bi-Te; possibly Sb-Cu_2Sb.

Acknowledgment

Acknowledgment is gladly made to Dr. O. E. Harder, under whose direction the research has been carried out; also to Mr. R. L. Dowdell, of the Department of Metallography, for his assistance in making the specimens.

DISCUSSION

Carl Benedicks,* Stockholm, Sweden.—There are so many interesting photomicrographs in this paper that I think there is reason for going slightly more into detail. Fig. 6, for instance, is an extremely beautiful and characteristic structure, and it would be of considerable interest if some explanation of this structure were given. What is the reason for a structure of this kind, very finely divided in the middle and coarser at the outside? Probably the structure is due to the fact that when solidification started in the middle the whole of this finely divided part came at once; then the heat of solidification made the cooling of the outer part much slower than the cooling of the center part.

In order to support this explanation I would refer to Fig. 20, which is a case that I studied some years ago. Symmetrically between two flat lammellae are two flat crystal colonies, built up by a finely divided eutectic structure, but in these crystals periodical differences occur. This must be because the solidification of the eutectic did not take place in a continual way but proceeded from the upper part so that at a given moment the boundary of the eutectic colony has been solidified in this way [demonstration]; the heat of solidification must have caused a definite arrest of the solidification; then a new portion crystallized, and so on. Thus, in order to explain these boundaries, we must consider the fact that the heat of solidification must be taken away before a new part of the eutectic is able to solidify. I think that the explanation of the picturesque structure in Fig. 6 will be a similar one. I should like to add, concerning the next to the last line on page 655, that those rounded eutectic colonies are also very typical in eutectic gray cast iron. There is some reason to believe that the rounded structure is related to the fact that the crystals of graphite themselves have a tendency for rounded forms.

* Director, Metallographic Institute of Stockholm.

Carle R. Hayward,* Cambridge, Mass.—I have obtained exactly the structures that Doctor Benedicks has shown in his sketches, in copper-silver alloys, which were melted under charcoal in graphite crucibles, taken from the furnace and cooled in air. I thought then that very likely the cooling would proceed as Doctor Benedicks has indicated, by radiation from the top, solidifying from the top and perhaps from the center rather than from the wells of the crucible. The walls were fairly thick and it is more than likely that there was more rapid cooling by radiation from the top, which would undoubtedly bring about the crystallization from various points. The structure was exactly the same as has been indicated in Figs. 5 and 6. I have wondered if that was the way in which the various specimens shown in the illustrations were prepared.

G. E. Dalbey,† East Berlin, Conn. (written discussion).—A recent publication covering a babbitt that is being put on the market states that a special method of alloying gives a decidedly superior structure to this alloy. Photomicrographs with magnification of 100 diameters show this special alloy to have a decidedly superior structure over a babbitt of the same analysis, the analysis in both cases being tin 88.9 per cent., antimony 7.4 per cent., and copper 3.7 per cent., which is an ordinary genuine babbitt.

The photomicrograph of the special babbitt shows a very fine structure with no decided crystals of the antimony-tin type. It shows all constituents of the babbitt to be thoroughly disbursed. The photomicrographs of the ordinary genuine babbitt shows the cubic crystals of tin-antimony and also shows a decided segregation of the constituents.

The Brinell hardness numbers, as follows, show the decided superiority of the special metal:

	At 70° F.	At 212° F.
Genuine babbitt	23 8	8.2
Special metal	23.8	12.7

The structure of this special babbitt is not destroyed by remelting and recasting, and it states in the publication that there are no special precautions to take in melting and casting this metal over what are used in handling ordinary babbitt. It is stated that owing to the elimination of the crystalline structure, the special babbitt possesses an unusual degree of plasticity. A sample of this metal rolled in a sheet to the thickness of about 0.01 in. shows considerable toughness. It is almost impossible to tear this sheet and it can be bent a great number of times without breaking. This rolling cannot be done with an ordinary babbitt. It is possible under some conditions to bring about a combination of two substances by

* Associate Professor of Metallurgy, Massachusetts Institute of Technology.
† Metallurgical Superintendent, Stanley Chemical Co.

the introduction of the third substance, which does not of itself enter into combination. Such a substance is known as a catalytic agent.

Can anyone suggest the means by which the properties above described in this special metal can be arrived at?

George F. Comstock,* Niagara Falls, N. Y. (written discussion).—The author shows some interesting photomicrographs, the metallographic technique being of very high order of excellence. The writer would question, however, the interpretation of Fig. 5, as given at the top of page 657, and also the reference to free cadmium crystals near the bottom of page 659 in the discussion of Fig. 16. Some alloys containing cadmium and tin have been studied here recently, and it has been found that cadmium is very readily and severely attacked by nitric acid, while tin is left comparatively bright. Primary crystals of cadmium had an elongated needle-like form in those alloys, and were darkened even before etching on account of a sort of tarnish acquired during polishing with rouge. Primary tin crystals, on the other hand, remained bright during polishing, and had a rounded form like the bright areas in the author's Fig. 16. The writer would suggest, therefore, that the light constituent in Figs. 5 and 16 might more probably be tin than cadmium, and would like to ask what evidence the author has to support the contrary interpretation as given in the paper.

C. H. Green (author's reply to discussion).—The original conclusion regarding the microconstituents of the cadmium-tin eutectic was based on etching tests rather than on any extended investigation of the system. It was observed that when pure cadmium was kept free from tarnish during polishing it was not easily attacked by nitric acid, concentrated acid being necessary to bring out the grain boundaries. Also, it was found that 10 per cent. HCl or a solution of stannous chloride, both of which are used to etch tin, gave the same results as found in Figs. 5 and 16. Also, Fig. 15 shows cadmium crystals untarnished by nitric acid. Further investigation, however, of several alloys of the cadmium-tin system seems to show agreement with Guertler's theoretical discussion[9] that when cadmium separates out as primary crystals, these crystals, because of the coalescing power of cadmium, are not closely surrounded with eutectic as is the case of primary tin crystals. This would indicate that the light phase in Fig. 16 is the tin-rich phase and that the cadmium-rich phase is the more rapidly attacked by the etching reagent. This coalescing power of one phase is well known in the arsenic-copper alloys. This question of the identification of the phases does not change the type of the eutectic pattern. It does, however, emphasize another factor, *i. e.* the coalescing power of the primary solid phase,

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* Consulting Metallurgist.

[9] *Int. Ztschr. Met.* (1911–12) **2**, 90.

which influences the form of the near-eutectic pattern. The author has not seen in any of the alloys examined, nor in published photomicrographs, the needle-like form of cadmium crystals mentioned by Mr. Comstock. The general experience has been that these crystals have a tendency to take a rounded form such as those shown by Guertler in the discussion mentioned.

Regarding Doctor Benedicks' discussion of Fig. 6, the author agrees with his explanation of the change in size of the particles. It seems likely that at the beginning of freezing there may have been a certain amount of supercooling and as a result when freezing began the nuclei number was very large; that is, the number of crystal nuclei formed per unit volume was large and as a result a very fine structure was produced. During the freezing of the eutectic, the heat of solidification was evolved, and it is entirely possible that there was even a slight increase in temperature. This would tend to reduce the nuclei number in the remaining melt; and having reduced the nuclei number and provided for a slower rate of cooling, the likely thing to expect would be increased size of particles. This apparently is what generally happens.

There seems to be no relation between the orientation of the specimen during cooling and the distribution of the fine and coarse particles in the eutectic. For example, specimens cooled in the crucible and sections cut perpendicular to the vertical axis show these typical colonies; other specimens cast in iron molds and the section cut through a vertical plane of the casting show the same structures. There is, however, a variation in the size of the colonies in different specimens and in different parts of a particular specimen, which is apparently influenced by the cooling. The above discussion seems to apply also to the remarks by Professor Hayward.

Determination of Structural Composition of Alloys by a Metallographic Planimeter

By E. P. Polushkin,* New York, N. Y.

(New York Meeting, February, 1925)

This work has for its purpose the establishment of a new method for determining the structural composition of alloys. The area occupied by a constituent on a few representative photomicrographs of the alloy is measured, by a planimeter, especially designed for metallographic work, and the volume and proportional weight of the constituent calculated.

Experiments have shown that the results are accurate enough to justify the application of the method to many problems in metallographic research instead of chemical analysis. The advantage of the method is the possibility of determining the amount of the constituents without separating them from the alloy; their composition may also be determined if the ultimate chemical analysis of the alloy is known.

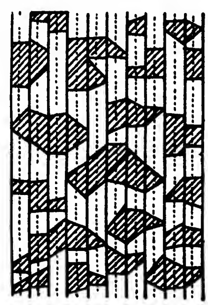

Fig. 1.—Part of photomicrograph on which total area of black figures is to be found.

Description of Planimeter

Suppose Fig. 1 represents a part of a photomicrograph on which the total area of the black figures is to be found. By a system of parallel lines drawn short equal distances apart all figures may be divided into trapezoids. As the area of a trapezoid is equal to its median multiplied by its altitude, the relation between the total areas of the black and the white figures comprised within each strip is equal to the relation between the sums of medians for these figures respectively. This is also true for the whole area of the photomicrograph. Therefore, to determine the total areas of the black and white figures we must first find the proportion between the sums of the medians and then divide the area of the whole photomicrograph in the same proportion.

* Instructor in Metallurgy, Columbia University.

The purpose of the planimeter is to measure the medians, or, as we shall call them, line segments, and to sum them up automatically. The planimeter is shown in Figs. 2 and 3. It consists of a stage *a* that has two

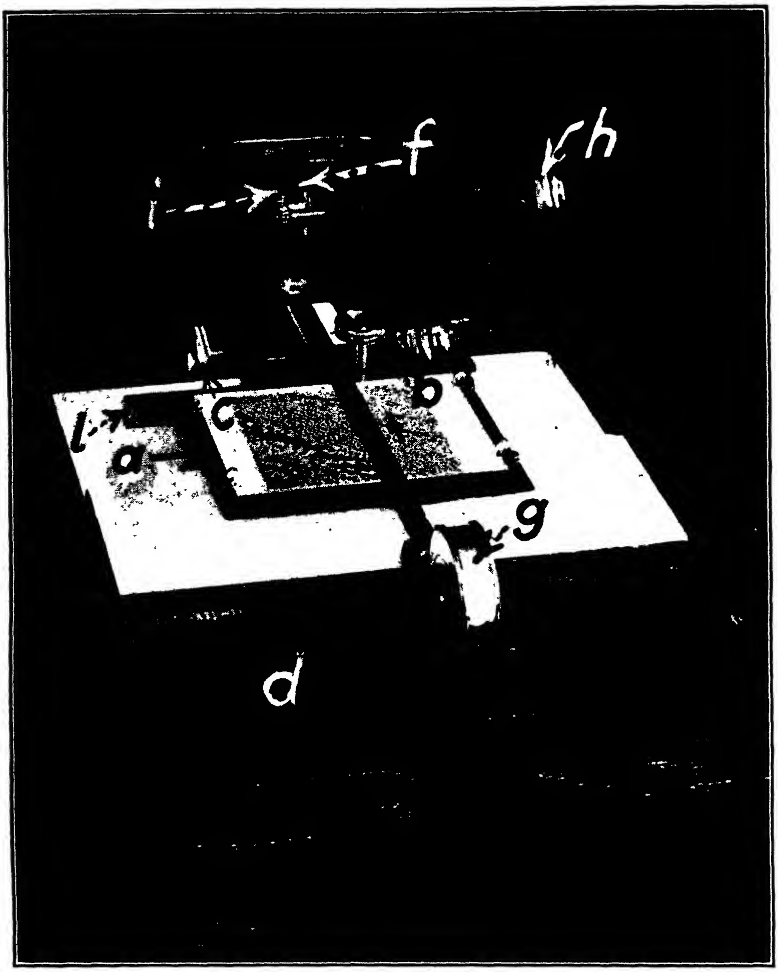

FIG. 2.—METALLOGRAPHIC PLANIMETER.

motions, at right angle to each other, both controlled by rack and pinion. The lateral motion is produced by rotating knob *b*, the forward-backward motion by rotating knob *c*, which is fixed on the base *d* of the apparatus, while knob *b* can move with the stage. Tape *e*, graduated in millimeters, has one end fixed to a drum *f* and the other end joined to a case *g*. By rotating knob *h*, which operates a pinion *i* and wheel, the tape may be wound on the drum; then its graduated edge passes over the figures on

the photomicrograph placed on the stage. Line *o* on the base serves as an index to show the exact position of the tape.

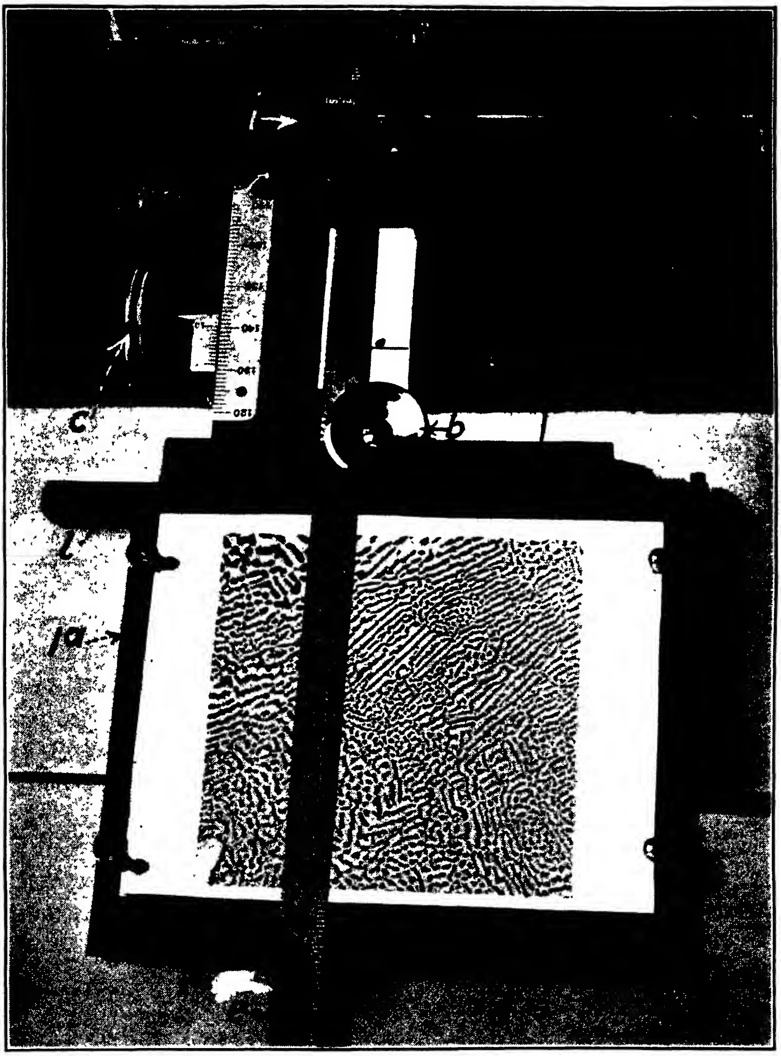

FIG. 3.—TABLE OF PLANIMETER.

The photomicrograph should be pasted to a glass plate, which is then fastened to the stage by four small screws. A magnifying glass placed above the stage makes small figures of the photomicrograph visible; it can be rotated around a pin so as to follow the stage in its motion.

Suppose that the edge of the tape crosses figures *A*, *B*, *C*, Fig. 4, and that line segments *ab*, *cd*, *ef* are to be measured and summed up. One

division on the tape is put opposite the index line o; this division is a starting number of the record and should be marked on a record sheet. The division on scale l, showing a lateral position of the stage, should also be noted. By rotating knob c the stage is moved, either forward or backward, until one of the divisions on the tape, say 570, coincides with the lower boundary of figure A. Then, by rotating knob h, the tape is moved until 570 coincides with the upper boundary b of figure A. The stage is moved again, and 570 is placed on the lower boundary C of figure B. Then the tape is moved until 570 reaches d, and so forth. In this procedure the tape is moved only when crossing figures and the stage when crossing the interstices between the figures. Consequently, the total length passed by the tape expresses the sum of all line segments of the recorded figures.

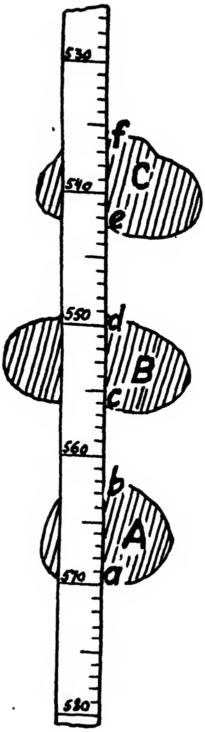

FIG. 4.—METHOD OF MEASURING AREAS OF PARTS OF PHOTOMICROGRAPHS.

A division on the tape which we follow in crossing the photomicrograph is called the *guiding mark*. If figures are not numerous and are spaced comparatively far apart, the guiding mark may be changed, the nearest division to the boundary of a figure being used in all cases; this will save unnecessary movement of the stage.

When the photomicrograph is once crossed from bottom to top, the stage must be moved sidewise for one division of scale l, and the operation just described is repeated along the new line of record. In this way the whole surface of the photomicrograph is passed over. If the length of the photomicrograph is n and the width m, all n crossings should be made equal in length to m. If the total area of the recorded figures is denoted as a_1, the whole area of the photomicrograph a, the total sum of line segments of the recorded figures l_1, and the total length of the record l, the following proportion holds true:

$$\frac{a_1}{a} = \frac{l_1}{l} \tag{1}$$

where $l = m \times n$ and l_1 represents the difference between the final and the starting divisions on the tape; *i. e.*, the relation between the total area of the recorded figures and the entire area of the photomicrograph equals the relation between the sum of line segments of these figures and the total length of the record. This is the first principle of the planimetric determination of area.

Calculation of Proportional Weight of Constituents in Alloys

It is further assumed that the volume v_1 occupied by a constituent is in the same relation to the entire volume v of the alloy as is the area of this constituent a_1 to the entire area a of a photomicrograph; viz.,

$$\frac{v_1}{v} = \frac{a_1}{a} = \frac{l_1}{l} \tag{2}$$

The correctness of this assumption was proved by the experiments, but it may be shown also by reasoning, similar to that which is applied in the deduction of formulas of volume in integral calculus.

From formula 2, the weight of the constituent may be calculated, if the specific gravities of this constituent and the alloy are known. Let w be the actual weight of the alloy; w_1, the actual weight of the constituent; W, the weight of the constituent, in per cent. of the alloy (the proportional weight); d, the specific gravity of the alloy; d_1, the specific gravity of the constituent.

Then
$$\frac{w_1}{w} = \frac{v_1 d_1}{vd} \text{ or } \frac{w_1}{w} = \frac{l_1 d_1}{ld},$$

and
$$W = \frac{100 l_1 d_1}{ld} \text{ per cent.} \tag{3}$$

If the specific gravity of an alloy is not known and the alloy has only two constituents, both of known specific gravity, another formula is needed. Formula 2 may be expressed also as

$$\frac{v_1}{v_2} = \frac{a_1}{a_2} = \frac{l_1}{l_2} \tag{4}$$

Where v_2, a_2 and l_2 are, respectively, the partial volume, the area, and the sum of line segments of the second constituent. Denoting the actual weight and the specific gravity of the second constituent by w_2 and d_2,

$$\frac{w_1}{w_2} = \frac{v_1 d_1}{v_2 d_2},$$

or
$$\frac{w_1}{w_2} = \frac{l_1 d_1}{l_2 d_2},$$

or
$$\frac{w_1}{w_1 + w_2} = \frac{l_1 d_1}{l_1 d_1 + l_2 d_2};$$

and
$$W = \frac{100}{1 + \frac{l_2 d_2}{l_1 d_1}} \text{ per cent.} \tag{5}$$

The value of l_2 is obtained by subtracting l_1 from the total length of record l.

When both constituents have the same specific gravity, formula (5) may be simplified as follows:

$$W = \frac{100\, l_1}{l} \text{ per cent.} \tag{6}$$

One of these three formulas 3, 5, and 6 was used for determining the proportional weight W of the constituent measured, the amount of the other constituent was calculated by difference.

In alloys with more than two constituents, the record should be taken, first, of one of the constituents and its proportional weight calculated by formula 3; then the second constituent must be recorded and calculated, and so on to the last one, which is determined by difference. Each consecutive operation may require a special etching for the separation of but one constituent each time. The specific gravity of all constituents and of the alloy itself must be known in this case.

Accuracy of Planimetric Method

To check the accuracy of the planimeter, a special test drawing was prepared with 40 per cent. of its area occupied by black figures and the remainder with white figures. All figures were small and varied in shape, size, and distribution. The results of determinations are given in Table 1.

Table 1.—*Test Drawing 3¼ by 4¼ In.; Exact Width of Area Occupied by Figures was 74.5 Mm.*

Record Number	Number of Crossings, n	Total Length of Record, l	Sum of Line Segments of White Figures	Proportional Area of White Figures in Per Cent., $\frac{100l_1}{l}$	Approximate Number of White Figures Intersected, F
1	12	74.5 × 12 = 894.0	546.0	61.1	
2	21	74.5 × 21 = 1,564.5	928.5	59.4	
3	20	74.5 × 20 = 1,490.0	883.0	59.2	420
4	37	74.5 × 37 = 2,756.5	1,660.5	60.2	740
4 records	90	6,705.0	4,018.0		

$$\text{Mean } \frac{100l_1}{l} = \frac{4018 \times 100}{6705} = 59.9 \text{ per cent.}$$

In Table 1, as in the others, l and l_1 are given in millimeters. As shown by this table, the accuracy of the individual records is about 2 per cent., but is naturally higher for the mean value of the total area. These and further experiments have shown that the accuracy generally depends on the following conditions:

1. The number of figures on the photomicrograph; the more numerous they are, the greater is the accuracy. This is true, however, only to a certain limit set by the size of the figures; if extremely small, they are not readily visible and cannot be recorded accurately. The major-

ity of figures in our determinations were, at least, 1 mm. in diameter, or larger.

2. The number of crossings; the larger the number, the greater is the accuracy.

3. Careful manipulation, by the operator, in bringing the guiding mark in exact coincidence with the boundary of figures.

4. The space between two consecutive crossings; the experiments proved that 1 mm. was too small, so 2 mm. was used between two crossings in all records. Of course, with the greater spacing a larger area of the photomicrograph may be covered by the same number of crossings.

5. The sharpness of the photomicrograph.

Conditions of Work

The operation of the instrument is very simple. When the record is being made, knob *h* is held in the right hand and knob *c* in the left. The lens placed above the photomicrograph must be large enough to cover a considerable area and should magnify from 2 to 3 diameters. Certain conditions of the preparation of the sample and the photomicrograph are very important. The sample should be truly representative for a given alloy and, if the composition and structure are varying, it must contain all possible variations.

The photomicrographs must represent an average structure; in any event, several photomicrographs should be taken from each sample. When the amount of a known constituent is to be determined, to find the chemical composition of an alloy, two or three photomicrographs are sufficient, if the alloy is homogeneous; but when an exact structural composition of an eutectic is sought, the number should be increased. We used from four to eight photomicrographs for each eutectic.

The method of etching should produce clear separation of one constituent, leaving all others in the uniformly colored background. In some cases a complex etching, which consists of two or more consecutive operations, is needed. A very deep etching is not desirable because it produces rough surface and shadows would increase or reduce the actual area of microconstituents.

When selecting the magnification, the aim should be to cover a larger area of the alloy by each photomicrograph; but a very low magnification should be avoided as it reduces the size of the particles to a limit of their visibility. In the experiments, 50 or 100 diameters were used in determinations of chemical composition of alloys; and 350 or 850 diameters in determinations of the structural composition of eutectics. The latter are usually very fine and at the same time possess great regularity in structure.

The time required to make the record depends on the size of the photomicrograph, the number of crossings, and the number of figures

on the photomicrograph. In the experiments, the time varied from 35 min. to 1 hr. If the width of the photomicrograph is from 75 to 80 mm., one crossing takes from 1 to 2 minutes.

Determination of Ultimate Composition of Binary Eutectics, When Chemical Analyses of Constituents Are Known

On account of their constancy in composition, eutectics have been selected for verifying the method. At the same time, it will be shown that this method may be conveniently used in quantitative analysis of eutectics. The structural composition of eutectics was found planimetrically and then their ultimate chemical composition was calculated.

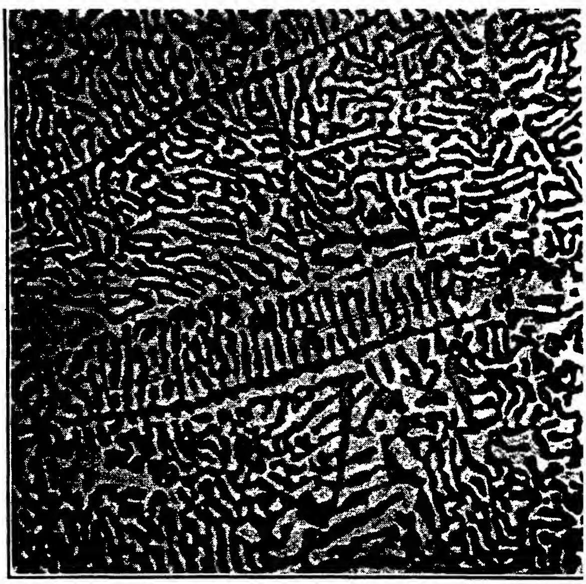

Fig. 5.—Bi-Sn eutectic. × 350.

The results are given in Tables 2 to 5. All lines are expressed in millimeters. Values of the specific gravity were taken either from Metalltechnischer Kalender by Dr. W. Guertler, 1923, or from Physikalisch-Chemische Tabbellen by Landolt-Bornstein, 4 Auflage, 1912.

Bi-Sn Eutectic

A small ingot was cooled in air; its composition was Bi, 58 per cent.; Sn, 42 per cent. It was etched by immersion in a mixture of ammonia and hydrogen peroxide for a few minutes; the bismuth remains white, the tin is darkened. Seven photomicrographs were taken, one of which is shown in Fig. 5. The results of the determination are given in Table 2.

TABLE 2.—*Bi-Sn Eutectic*

Photo-micro-graph	Number of Crossings, n	Total Length of Record, l	Sum of Line Segments of Dark Figures, l_1 (Sn)	$l - l_1 = l_2$ (Bi)	$\frac{l_2}{l_1}$	Approximate Number of Dark Figures Intersected, F (Sn)
a, ×150	30	2,370	1,136.0	1,234.0	1.09	
b, ×150	25	1,950	983.0	967.0	0.98	1,000
c, ×350	30	2,280	1,102.5	1,177.5	1.07	720
d, ×350	30	2,250	1,087.0	1,163.0	1.07	630
e, ×350	30	2,250	1,133.0	1,117.0	0.99	780
f, ×350	30	2,238	1,113.0	1,125.0	1.01	870
g, ×350	30	2,250	1,160.0	1,090.0	0.94	
7 photographs		15,588	7,714.5	7,873.5		
7 records		$\frac{l_2}{l_1} = \frac{7873.5}{7714.5} = 1.02$				

The value of $\frac{l_2}{l_1}$ was calculated for each record in order to see the accuracy of the individual determinations. The final value, however, was found by dividing the sum of all numbers in column l_2 by the sum of all numbers in column l_1.

For calculating the proportional weight of tin in eutectic, formula 5 was used. According to Lepkowsky (1908),[1] the solubility of tin in bismuth at room temperature is about 0.5 per cent., and the solubility of bismuth in tin is negligible. We can assume that in small ingots cooled in air the Bi-Sn eutectic consists of practically pure bismuth and tin. The specific gravity d_1 of tin is 7.28; the specific gravity d_2 of bismuth is 9.80; $\frac{d_2}{d_1} = 1.35$.

$$\frac{l_2}{l_1} \times \frac{d_2}{d_1} = 1.38$$

Amount of tin W is $\frac{100}{2.38} = 42$ per cent.; amount of bismuth, 58 per cent. If bismuth dissolves 0.5 per cent. tin, then 58 per cent. bismuth contains $58 \times 0.005 = 0.3$ per cent. tin; therefore, Bi-Sn eutectic contains from 42 per cent. to 42.3 per cent. tin. The generally accepted composition of this eutectic is 42 per cent. tin and 58 per cent. bismuth.

Bi-Sn Eutectic in the Ternary Alloy of Bi-Sn-Pb

Two small ingots were taken for determination, both of the same composition: bismuth, 75 per cent.; tin, 15 per cent.; lead, 10 per cent. The polished surfaces were etched with HNO_3, 5 per cent. solution in alcohol. A fine mixture of bismuth and tin, surrounding solid crystals

[1] Guertler: Metallographie I Band, I Teil, 742.

of bismuth and having the same outlines, is generally assumed to be a binary Bi-Sn eutectic (Fig. 6). The planimetric determination showed, however, that its composition is far different from the composition of the normal Bi-Sn eutectic; this may be seen from Table 3.

FIG. 6.—Bi-Sn EUTECTIC IN TERNARY Bi-Sn-Pb ALLOYS. × 150.

TABLE 3.—*Bi-Sn Eutectic in Ternary Bi-Sn-Pb Alloy*

Photomicrograph	n	l	l_1 (Sn)	l_2	$\frac{l_2}{l_1}$	F (Sn)
a, ×350	30	2,268.0	623	1,645.0	2.64	660
b, ×150	46	2,143.5	578	1,565.5	2.71	
c, ×350	33	2,508.0	923	1,585.0	1.72	380
d, ×150	46	2,481.0	750	1,731.0	2.31	
e, ×350	30	2,241.0	882	1,359.0	1.54	510
5 photomicrographs		11,641.5	3,756	7,885.5		
5 records		$\frac{l_2}{l_1} = \frac{7885.6}{3756} = 2.1$				

The value of $\frac{d_1}{d_2}$ was already found to be 1.35.

$$\frac{l_2}{l_1} \times \frac{d_2}{d_1} = 2.1 \times 1.35 = 2.83$$

The amount of tin is $W = \frac{100}{3.83} = 26.1$ per cent.

It is very probable that the rim of bismuth crystals in the ternary eutectic is not a binary eutectic of any kind, but a skeleton of a crystal with varying composition. Such skeletons can be found in other alloys.

In Fig. 6, the Bi-Sn eutectic does not occupy the whole area of the photomicrograph. In such a case, the total length l of record cannot be calculated as the product of the length of crossing by the number of crossings; it must be determined by a preliminary experiment in which the sum of the line segments of the whole area of the eutectic is found. Then the usual record of one of the constituents in the eutectic is taken. This method was always used in similar cases.

Ag-Cu Eutectic

A small ingot was cooled in air; its composition was Ag 72.5 per cent., Cu 27.5 per cent. It was etched by immersion in a mixture of ammonia

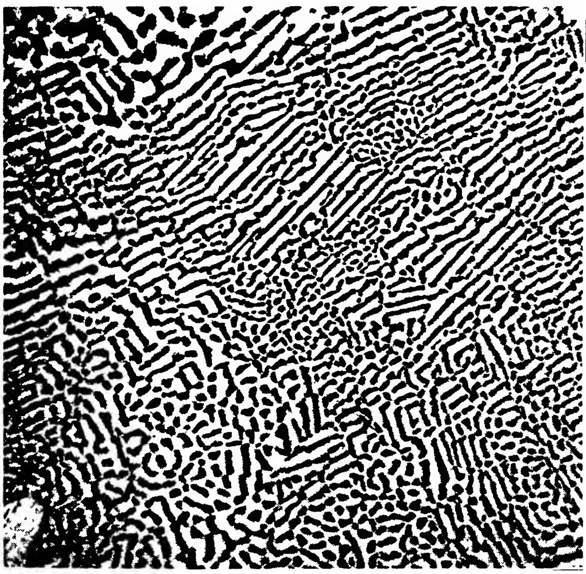

FIG. 7.—Ag-Cu EUTECTIC. × 350.

and hydrogen peroxide for 10 to 15 sec. Six photomicrographs were taken; a typical photomicrograph is given in Fig. 7. Silver appears white and copper dark. The results are given in Table 4.

According to Lepkowsky's diagram, the saturation points are 7 per cent. copper and 6 per cent. silver. These values were found for very slow cooling; but if the alloy is cooled in air, they would be much lower. Prof. William Campbell states that in such cases the solubilities are not over 1 per cent. on each side. We found a fairly noticeable amount of eutectic in an ingot with 97 per cent. silver that was cooled in air.

TABLE 4.—*Ag-Cu Eutectic*

Photomicrograph	Number of Crossings, n	Total Length of Record, l	Sum of Line Segments, l_1 (Cu)	$l - l_1 = l_2$	$\frac{l_2}{l_1}$	Approx. Number of Figures Intersected, F (Cu)
a, ×850	30	2,280	688	1,572	2.31	630
b, ×850	30	2,280	692	1,588	2.29	480
c, ×850	30	2,280	653	1,627	2.49	390
d, ×850	30	2,280	682	1,598	2.34	330
e, ×350	30	2,250	645	1,605	2.49	1,080
f, ×350	30	2,250	695	1,555	2.24	600
6 photomicrographs		13,620	4,055	9,565		
6 records		$\frac{l_2}{l_1} = \frac{9565}{4055} = 2.36$				

Assuming that both solubilities are equal to 1 per cent.

Specific gravity[2] of copper d_1 containing 1 per cent. silver $= a + bx = 8.93 + 0.014 \times 1 = 8.94$.

Specific gravity of silver d_2 containing 1 per cent. copper $= a + bx = 10.50 - 0.014 \times 1 = 10.49$.

Then $\frac{u_2}{d_1} = 1.17$, and $\frac{l_2}{l_1} + \frac{d_2}{d_1} = 2.36 \times 1.17 = 2.76$; then, from formula 5, the amount of copper solution $W = \frac{100}{3.76} = 26.6$ per cent.

26.6 per cent. copper contains $26.6 \times 0.01 = 0.27$ per cent. silver
73.4 per cent. silver contains $73.4 \times 0.1 = 0.73$ per cent. copper.

Eutectic contains $26.6 - 0.27 + 0.73 = 27.1$ per cent. copper and 72.9 per cent. silver. Lepkowsky and other investigators found that eutectic contains 28 per cent. copper.

As the constitutional diagrams are always drawn for very slowly cooled alloys; the question arises as to how rapid cooling would change the nature of eutectic. It may be assumed that three cases are possible: First, the proportion of the constituents in the eutectic remains the same but the chemical composition of each constituent is changed; therefore, the ultimate chemical composition of the eutectic is also changed. Second, the chemical composition of the constituents remains the same, but the proportions are changed. Third, both the chemical compositions and the proportions are changed. We have no evidence which of these three cases occur in silver-copper alloys.

Iron-phosphide Eutectic in Gray Cast Iron

Sample A contained total carbon 3.04 per cent., phosphorus, 1.47 per cent, silicon 2.89 per cent., manganese 1.11 per cent., sulfur 0.08 per

[2] W. Guertler: Metalltechnischer Kalender.

cent.; two photomicrographs *a* and *b* were taken. Sample B contained total carbon 3.46 per cent., phosphorus 0.90 per cent., silicon 2.19 per cent., manganese 0.81 per cent., sulfur 0.16 per cent.; four photomicrographs *c*, *d*, *e*, *f* were taken. Both samples were deeply etched with picric acid.

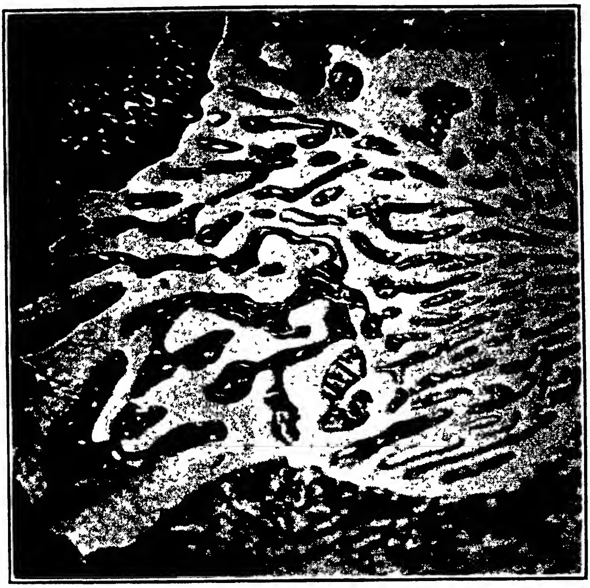

FIG. 8.—IRON-PHOSPHIDE EUTECTIC IN GRAY CAST IRON. × 850.

A typical photomicrograph is shown in Fig. 8. The results are given in Table 5.

TABLE 5.—*Iron-phosphide Eutectic in Gray Cast Iron*

Photomicrograph	n	l	$l_1(Fe_3P)$	l_2	$\frac{l_2}{l_1}$	$F\ (Fe_3P)$
a, ×850	23	734.0	505.0	229.0	0.45	
b, ×850	35	695.5	521.0	174.5	0.34	200
b, ×850	35	695.5	510.0	185.5	0.36	
b, mean	35	695.5	515.5	180.0	0.35	
c, ×850	32	1,166.0	835.0	331.0	0.40	240
d, ×850	38	1,046.0	737.0	309.0	0.42	230
e, ×850	38	1,943.0	1,276.0	667.0	0.52	420
e, ×850	38	1,948.0	1,276.0	669.0	0.53	
e, mean	38	1,945.0	1,276.0	669.0	0.52	
f, ×850	38	850.0	610.0	240.0	0.40	230
6 photomicrographs		6,436.5	4,478.5	1,958.0		
8 records						

$$\frac{l_2}{l_1} = \frac{1958}{4478.5} = 0.44$$

In summing up columns l, l_1, and l_2, we have taken the mean value of these lines, when double records were taken, because each photomicrograph represents a point in the alloy, and, therefore, in the calculation of the average composition, we must count each photomicrograph as a unit.

As shown in Fig. 8, phosphide eutectic consists of two constituents, the white and the dark.

"Stead writes that in very gray phosphoretic metals, the carbon diffuses out of it and a binary eutectic of Fe_3P and iron containing in solution a little phosphorus is formed."[3] On the other hand, microscopic examination reveals that the darker constituent has an appearance of pearlite. For these reasons, in these calculations, we shall assume that the eutectic is a mixture of Fe_3P with either ferrite or pearlite.

Specific gravity[4] of Fe_3P, $d_1 = 6.74$

Specific gravity of Fe, $d_2 = 7.86$

Specific gravity of pearlite may be calculated by the formula:

$$D = a + bx = 7.86 - 0.35 \times 0.85 = 7.56$$

but this gives a value that is evidently too low. If we consider pearlite as a mixture of seven parts of iron with one part of cementite (specific gravity 7.07), we can calculate its density as a mean of the densities of the two constituents:

$$\frac{7.86 \times 7 + 7.07}{8} = 7.76$$

which is in better accordance with the observed values for steel.

In the case of ferrite, $\frac{d_2}{d_1} = \frac{7.86}{6.74} = 1.17$

In the case of pearlite, $\frac{d_2}{d_1} = \frac{7.76}{6.74} = 1.15$

$$\frac{l_2}{l_1} \times \frac{d_2}{d_1} = 0.44 \times 1.17 = 0.515$$

$$= 0.44 \times 1.15 = 0.506$$

The difference is so small that 0.51 can be taken for each.

The amount of Fe_3P in the eutectic $W = 100 \div 1.51 = 66.2$ per cent.

The amount of phosphorus in phosphide of iron can easily be calculated:

$$\frac{31.04 \times 100}{55.84 \times 3 + 31.04} = 15.63 \text{ per cent.}$$

66.2 per cent. of Fe_3P contains $66.2 \times 0.156 = 10.3$ per cent. phosphorus. Therefore, according to planimetric determination, the eutectic contains 10.3 per cent. phosphorus.

[3] A. Sauveur: "The Metallography and Heat Treatment of Iron and Steel," 2d ed., 390–1.

[4] Landolt-Börnstein: Physik.-Chem. Tabellen, 4 auflage.

Eutectic of White Cast Iron

Determinations were made on two samples; the first was a piece of chilled iron consisting almost entirely of eutectic. Four photomicrographs, at 350 diameters, were taken. The second was white iron of the following composition: Combined carbon 3.80 per cent.; graphite, trace; silicon 0.57 per cent.; manganese 0.20 per cent.; phosphorus 0.31 per cent.; sulfur, 0.096 per cent. Five photomicrographs, at 350

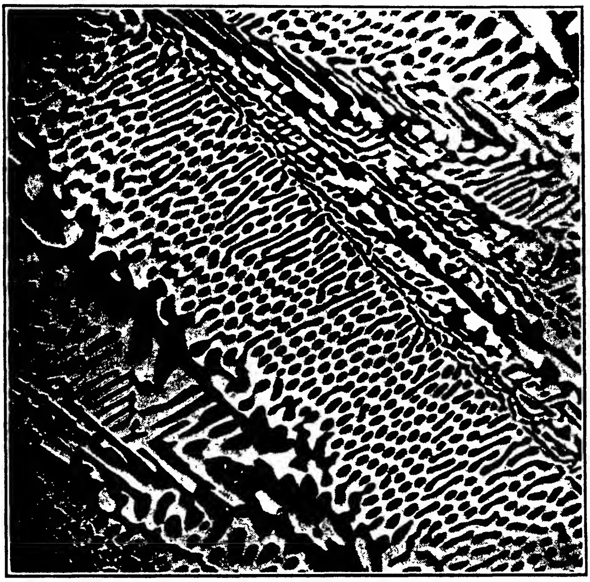

FIG. 9.—EUTECTIC OF WHITE CAST IRON. × 350.

diameters, were taken. Both samples were etched with picric acid. A typical photomicrograph is shown in Fig. 9.

The mean value of $\frac{l_2}{l_1}$ for ten records was 0.68. Here l_1 denotes the sum of line segments of cementite and l_2 the same of pearlite, found by difference.

$$\text{Amount of cementite } W = \frac{100}{1 + \frac{l_2 d_2}{l_1 d_1}} = 57.1 \text{ per cent.}$$

$$\text{Amount of pearlite} = 42.9 \text{ per cent.}$$

Carbon content in cementite was 57.1 × 0.067 = 3.83 per cent.
Carbon content in pearlite was 42.9 × 0.0085 = 0.37 per cent.
Total 4.20 per cent.

Eutectoid in Bronze

A sample of bell metal with 20 per cent. tin was etched with Grard's solution and seven photomicrographs at 850 diameters were taken; one is shown in Fig. 10. The mean value of $\frac{l_2}{l_1}$ for seven records was 3.17. l_1 denotes the sum of line segments of alpha and l_2 of delta.

It is generally assumed that delta contains 31.8 per cent. of tin. The concentration of tin in alpha varies with the rate of cooling, from 6 to 13 per cent. In the case of 6 per cent., the specific gravity of alpha, calculated by the formula $d_1 = a + bx$ is 8.78. As the specific gravity of

Fig. 10.—Eutectoid in bronze. × 850.

delta d_2, is 8.14, the relation $\frac{d_2}{d_1} = 0.95$, and the amount of alpha

$$W = \frac{100}{1 + \frac{l_2 d_2}{l_1 d_1}} = 25.3 \text{ per cent.}$$

Then the amount of delta equals 74.7 per cent.

Total amount of tin in alpha is 25.3 × 0.06	=	1.52 per cent.
Total amount of tin in delta is 74.7 × 0.318	=	23.75 per cent.
Total tin in eutectoid	=	25.27 per cent.

In case of 13 per cent., similar calculations give 26.99 per cent. as the total amount of tin in the eutectoid.

We have considered two extreme cases, while the real concentration of tin in alpha in any particular bronze may be between 6 and 13 per cent., then the total tin in the eutectoid would be very near 26 per cent., in full accordance with the generally accepted composition of this eutectoid.

Determination of Chemical Analysis of Alloys with Known Constituents

If the chemical composition of the constituents is known, the chemical analysis of the alloy may be determined by the same method as was applied to the eutectics; viz., first, the area of each constituent is determined by the planimeter and then the proportional weight of each is

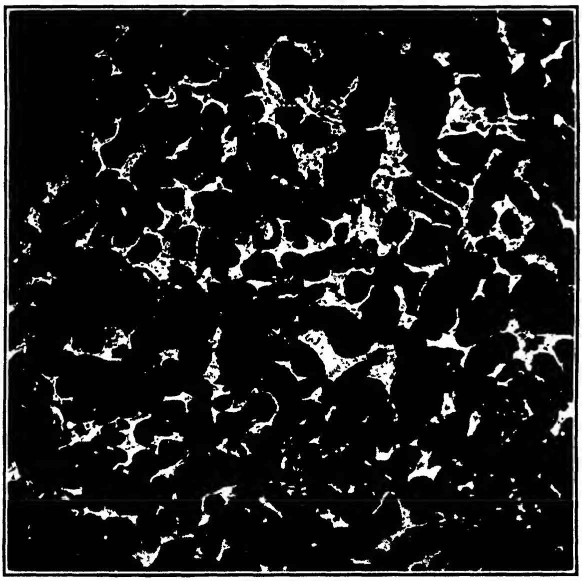

Fig. 11.—Phosphide eutectic in gray cast iron. × 100.

calculated by formulas 5, 3, or 6. We used this method for determination of carbon in steels and cast iron, phosphorus in gray cast iron and in phosphor-copper, and so forth. Some of the results are given in Table 6.

Reviewing all cases of the determination of carbon in steel, it may be stated that carbon was invariably found lower than it was shown by the chemical analysis. We have no explanation to offer for this except that the carbon content in pearlite is probably higher than 0.85 per cent., as was accepted in our calculations.

The sample of gray cast iron with high phosphorus was etched deeply, first, with picric acid and then with Le Chatelier-Dupuy reagent. The phosphide eutectic then became clearly visible on a dark field.

TABLE 6.—*Determination of Carbon and Phosphorous in Steel, Cast Iron and Phosphor-Copper*

Description of Samples	Number of Photo-micro-graphs and Magnifi-cations	Total Number of Cross-ings	Total Length of All Records	Total Number of Figures Inter-sected	Percentage of the Chemical Elements Found	
					Plani-metric-ally,	By Chemical Analysis,
					C	C
Rolled steel	4 ×50	60	4,500	1,750	0.20	0.24
Crucible-steel ingot, Mn 0.22 per cent., Si 0.11 per cent.; heated to 1000° C. and slowly cooled	2 ×50	60	4,504	825	0.46	0.50
Crucible-steel ingot, Mn 0.25 per cent., Si 0.10 per cent.; treated as above	4 ×50	148	11,070	1,400	0.74	0.78
Crucible-steel ingot, Mn 0.28 per cent., Si 0.22 per cent.; treated as above	2 ×100	88	6,535	1,000	1.24	1.32
White cast iron, graphite trace, Si 0.57 per cent., Mn. 0.20 per cent., P 0.31 per cent., S 0.096 per cent	2 ×150	60	4,770	1,850	3.93	3.80
					P	P
Gray cast iron, total C 3.04 per cent., Si 2.89 per cent., Mn 1.11 per cent., S 0.081 per cent	4 ×100	138	10,407	1,200	1 43	1.47
Phosphor-copper, Cu 89.71 per cent., P 10.33 per cent	3 ×50	90	6,756	1,860	10.38	10 33

DETERMINATION OF THE CHEMICAL COMPOSITION OF UNKNOWN CONSTITUENTS IN BINARY ALLOYS

Supposing we have a series of binary alloys with two constituents, both of unknown composition. We select two alloys with a possibly larger difference in proportion of one of the constituents and analyze them planimetrically. First, the specific gravity of the constituents must be found. It may be calculated, after the specific gravities d_1 and d_2 of both alloys have been determined by weighing and the proportional volumes of each constituent have been found planimetrically, from two equations:

$$a_1x + (100 - a_1)y = 100d_1 \tag{7}$$
$$a_2x + (100 - a_2)y = 100d_2 \tag{7a}$$

where a_1 and a_2 denote the proportional volumes of the first constituent in the first and in the second alloys, respectively. The proportional volumes of the second constituent are expressed as the differences; x and y are the specific gravities of the first and the second constituents.

When the specific gravities are determined, two other equations must be composed, from which the percentage Z of one of the chemical elements in the first constituent, and the percentage U of the same element in the second constituent may be found.

$$A_1Z + (100 - A_1)U = 100n_1 \tag{8}$$
$$A_2Z + (100 - A_2)U = 100n_2 \tag{8a}$$

A_1 and A_2 denote the proportional weights of the first constituent in the first and in the second alloy, respectively. The proportional weights of the second constituent are represented by the differences, n_1 and n_2 are the percentages of the chosen element in the first and in the second alloy, respectively, found by chemical analysis. When Z and U are determined, the percentages of the second chemical element are obtained by subtraction of Z and U from 100.

If one of the constituents contains only one element, formulas 8 and 8a will be reduced to a simpler form:

$$A_1Z = 100n_1 \tag{9}$$
$$A_2Z = 100n_2 \tag{9a}$$

Dividing one equation by the other, we have

$$\frac{A_1}{A_2} = \frac{n_1}{n_2} \tag{10}$$

that is, the amount of the constituent containing both elements is proportional to the percentages of the element present in this constituent only. Such a case we have, for instance, in hypoeutectoid steel where the amount of pearlite is proportional to the percentage of carbon.

Similar formulas may be composed, also, for the ternary alloys.

DISCUSSION

H. S. Rawdon,* Washington, D. C. (written discussion).—Any one who has occasion to make planimetric measurements by the ordinary means in metallographic work will welcome the simplification here described. Although there may be a difference of opinion concerning the utility of the planimetric method as a general means of metallographic study, no one questions the decided advantage and the almost absolute necessity of the method in certain cases.

Some consideration has been given by the writer to the possibility of a further simplification which would do away with the tedious eye-straining work that any planimetric method necessarily involves. The possibility of a photometric method has received some attention. This would involve a measurement of the average brightness of the micrograph under

* Physicist, Bureau of Standards.

study, or perhaps the average density of a transparency of the micrograph as shown by the transmission of light through it, and its relative brightness (or transmission) as compared with similar plates developed so as to show the same intensity as that of each of the constituents in the structure that is being studied; for example in Fig. 5, Bi-Sn eutectic, two reference plates, one of the intensity of the light-colored areas, and one corresponding to the dark constituent.

Many objections can be raised to any such method, however, the foremost being the elimination of the human element, which is so necessary in the study and interpretation of micrographic data. For example, accidental variations in the shading of the plate as a whole (Figs. 5 and 8) or of different constituents caused by non-uniform illumination could not be taken account of by such a method, as would naturally be done by one using any planimetric device. This might cause serious error in the results. The preparation of the necessary comparison plates would undoubtedly require considerable practice and skill and it is questionable whether any material saving in time could be effected by any such method.

On the whole the author's modification of the usual planimetric method seems to be a decided simplification and at the same time it retains the necessary human element. The practical applications of the method, however, are so limited in number that perhaps attempts at further simplification would not be warranted.

A word of caution as to the practical application of the planimetric method may not be amiss. This can best be illustrated by example. If one were to estimate, as the author has done, Table 6, planimetrically the carbon content, of two hypoeutectoid steels of the same carbon content but differing considerably in manganese, both being in the annealed condition, of course, the results would undoubtedly indicate a wide difference in the apparent carbon content, as shown in a publication by the writer several years ago.[5] An increase in the manganese content of a hypoeutectoid steel is ordinarily equivalent, so far as the structure is concerned, to an increase of carbon. A 0.45 per cent. carbon steel containing only a trace of manganese was shown to have a decidedly different structure from a 0.45 per cent. carbon steel having a higher manganese content, say 1.3 per cent., although both were annealed by heating to a temperature of 750° C. and allowed to cool within the furnace.

The point is that the full-annealing treatment is not the same for the two steels. A treatment that would result in a condition of structural equilibrium for the steel of lower manganese content will not do so for the other. The point of general application must be borne in mind with

[5] H. S. Rawdon and F. Sillers, Jr.: Effect of Manganese on the Structure of Alloys of the Iron-carbon Series. Bur. of Stand. *Sci. Paper* 464.

any alloy, particularly as "unknown;" *i. e.*, Is the alloy in a condition of structural equilibrium?

P. N. Chirvinsky,* Novocherkask, Russia (written discussion†).—Planimetric measurements have been quite extensively used in petrography for determination of the composition of rocks. As the author gives no reference to the bibliography on this subject, I would say that the principle of the planimetric method was first described by the Austrian geologist Rosiwal many years ago. Later, Professor Hirschwald constructed a special planimetric eyepiece, which is now being made by optical firms of Fuess and Seibert, in Europe. This eyepiece was used by me (as well as by many others) in researches on the composition of rocks with quite satisfactory results.

Another method of the geometrical analysis was introduced in France by Delesse in 1848. It consists in weighing the paper cuts representing the figures of one of the constituents of a rock and comparing the weight with the total weight of the drawing or photograph representing the structure.

I have been using these methods for about 20 years and found them very useful in petrographic research. The practical side and the details of measurements are given in my book[5] on quantitative mineralogical composition of granites. Of course the same methods could be applied to the problems of quantitative analysis in metallurgical research, as I pointed out in 1908. For instance, the mineralogical composition of dinas bricks used in the construction of steel furnaces cannot be determined by chemical analysis as dinas consists of two minerals, quartz and tridymite, having exactly the same composition, so that the proportion between these two minerals can only be found by planimetric method.

Similar problems are frequently met with in the study of the composition of rocks. It is sufficient to refer to pyrrhotite, the composition of which is sometimes given by the authors in formulas different from FeS while it is possible to prove by planimetric method that it corresponds exactly to the formula FeS and that the excess of sulfur in some samples is due to the presence of isolated crystals of pyrite.

Quite recently I have been using methods of Delesse and Rosiwal in studying the composition of coarse granular meteorites known as pallasites. My usual practice is to make the measurements on three perpendicular sections of the sample in order to have various intersections of crystals. This practice may be recommended, especially when the crystals have uniform orientation in space, as for instance, in a piece of mica.

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* Translation by E. P. Polushkin.

† Professor of Applied Geology and Dean of Mining Faculty, Don Polytechnical Institute.

[6] See reference by G. F. Kunz in *Science* (1911) 11, 348.

E. P. Polushkin (author's reply to discussion).—In regard to the statement that the practical applications of the planimetric method are very limited, I would say that there is no reason why this method could not be extensively used in metallographic research. An ordinary planimeter is not practicable for metallographic determinations, but a planimeter suitable for metallographic work may render a valuable service to the research on alloys.

At present, two methods are used for the determination of the chemical composition of the constituents in alloys. The first is based on differential solubility of the constituents in chemical reagents. The alloy is dissolved in a certain reagent, which dissolves all constituents but one, which is separated out and may be analyzed. But to find such a reagent is a difficult task. The other method is to prepare a series of alloys, which are examined under the microscope and the one found to contain only one constituent is analyzed. In this case the difficulty lies in the exact adjustment of the chemical composition in order to have but one constituent without a trace of any other.

By the planimetric method the composition of microconstituents can be determined without separating them, either chemically or mechanically, from the alloy, and the results obtained by this method may be as accurate as those obtained by chemical analysis. In many cases, when two or three unknown constituents are present in each alloy of the series, it is the only method available for determination of their chemical composition.

Delesse's method was used in metallography for the determination of the proportion of copper oxide eutectic in copper. Some other methods were also advocated. Yet the practical application of planimetric methods did not meet with success in metallography, because of the many tedious operations involved in order to secure accurate results. To make the planimetric method efficient, it was necessary to introduce some automatic device for measuring small areas. It was with this purpose in view that I constructed a planimeter which is adapted to the determination of the summarized area of small figures. From six to eight photomicrographs, containing about one thousand figures each, can be recorded with this instrument in a day, *i. e.*, up to 8000 small areas measured in 8 hours.

Tantalum, Tungsten and Molybdenum

By E. W. Engle,* North Chicago, Ill.

(New York Meeting, February, 1925)

For several years the Fansteel Products Co. has been engaged in the production and development of various of the rarer metals. It is at present engaged in the commercial production of tantalum, tungsten, and molybdenum in a very high state of purity. The information contained in this paper is partly a general compilation from various sources and partly information obtained as a result of recent years of work in the laboratory of this company.

Tantalum, tungsten, and molybdenum form a group peculiar to themselves among the commercially available metals. Their very high melting points (tantalum 2770° C., tungsten 3350° C., and molybdenum 2550° C.) set them apart so far as the metallurgical processes for their production are concerned. Further, when properly prepared and treated they will stand a somewhat unusual degree of cold work, that is work below the temperature at which marked crystal growth takes place. Such cold-worked metal may show a high tensile strength; tantalum to 130,000 lb. per sq. in., tungsten to 490,000 lb., and molybdenum to 260,000 lb., in the form of fine wire.

In physical appearance, these metals are not unlike some steels; they may be better described by saying that polished tantalum somewhat resembles lead; polished tungsten, iron; and polished molybdenum, nickel. The polished surfaces of all three remain untarnished in ordinary air. Air containing corrosion-producing impurities will, in general, show molybdenum the least resistant to corrosion and tantalum the most resistant. Molybdenum has, however, a high degree of resistance to corrosion by hydrochloric acid, a property that should render it of commercial interest. On the other hand, it is markedly attacked by some of the weaker organic acids.

The three metals oxidize rapidly when heated at or above a dull red in air. This feature limits their use in many applications where their high melting point and strength make them appear usable. Tungsten and molybdenum, at red heat, are quite inert to hydrogen and nitrogen; while tantalum has a rather remarkable affinity for all the ordinary gases, which results in its becoming embrittled in their presence. This

* Metallurgist Fansteel Products Co., Inc.

TABLE 1.—*Data Concerning Some Metals*

	Tungsten	Tantalum	Molybdenum	Platinum	Copper	Nickel
Atomic number	74	73	42	78	29	28
Atomic weight	184	181.5	96	195.2	63 6	58.7
Density	19 6	16 6	10.2	21.4	8.80	8.84
Atomic volume	9.4	10.9	8 8			
Tensile strength, lb. per sq. in.	490,000	130,000	260,000	54,000 42,000	62,000 35,000	120,000 hard 70,000 annealed
Compressibility per kg. per sq. cm.	0.28×10^{-6}	0.50×10^{-6}	0.47×10^{-6}		0.76×10^{-6}	
Brinell hardness	290	45 9	147	90 hard 35 annealed		350 hard 90 annealed
Scleroscope hardness	40	10	12	14 hard 8 annealed		45 hard 10 annealed
Young's modulus of elasticity kg. per sq. mm.	42,200	19,000				22,000
Melting point, degrees C	3,350	2,770	2,550	1,755	1,083	1,452
Boiling point, degrees C.	5,830		3,617	3,907	2,310	
Vapor pressure	6.45×10^{-12} mm. 1,727° C 0 00114 mm. at 2,727° C.		$6,430 \times 10^{-12}$ mm. at 1,517° C	107×10^{-6} at 1,727° C	0 001 mm. at 1,080° C.	
Heat of vaporization	$217,800^{-1}.8T$ cal.				75,000	
Specific heat, cal. per gm. per degree.	0 034	0 0365	0.072	0 0323	0.0936	0.1084
Linear coefficient of expansion per degree C.	4.3×10^{-1}	7.9×10^{-6}	5.15×10^{-6}	8.84×10^{-6}		13×10^{-6}
Thermal cond., in cal. per c c	0 35	0.130	0 346	0 1664	0.7198	0 140
Heat of combustion, cal. per gm	1,047	1,147	1,740	87.1	593	987
Heat of combustion, cal. per gm., molecule to oxide	192 648	301 500	167 000	17,000	37,700	57,900
Temp. coefficient of resistance	0 0051	0 00335	0 005	0.0039	0.00393	0 0066
Elec. resistance microhm per c. c. at 25° C						
Annealed	5 2	14.6	4 8	9.97	1.87	6.4
Unannealed	6 2		5.6			
Magnetic susceptibility, $\times 10^6$	0.22	0 8	0 04	0.80	0.085	
Electrochem. equiv., mg. per coulomb	0 3173	0.3762	0 1658	0.3371	0.3294	0.3040
Refractive index	2.76	2.05				
Thermoelectric e.m.f. against copper, microvolts per degree	4.5 (above 200° C)	4.1		13.3	0.0	25

gas-absorbing power of tantalum has been put to practical use as a "clean-up" in vacuum tubes. It might also be well worth while to study the catalytic action of tantalum. It absorbs gases at red heat and liberates them at incandescence.

Table 1, which is largely a compilation from various available sources, gives a ready comparison between the physical and electrical properties of those three metals and platinum, copper, and nickel.

The high melting points of the metals, combined with their valuable physical properties and the fact that they are all capable of being produced as fine wires, have resulted in their being commercialized as constructional material in incandescent lamps, radio vacuum tubes, x-ray tubes, and similar devices.

Tantalum has a much greater electrical resistance than the other two. On the other hand it has a smaller temperature coefficient, which, to some extent, offsets this difference at higher temperatures. Molybdenum, at low temperatures, has a relatively high vapor pressure, so high in fact that in the production of incandescent lamps it is necessary to limit rigorously the allowable molybdenum content in the tungsten filament to prevent the bulb from becoming blackened with volatilized molybdenum, which would result in great decrease of light efficiency.

The metals are not very hard, despite a quite popular belief to the contrary. This belief seems to have risen from early published works describing experiments with impure materials. Relatively small quantities of some impurities affect, to a considerable degree, the properties of these elements. Their tendency to absorb carbon with the formation of brittle material is quite marked; it is, therefore, necessary to exclude carbon-containing materials during the hot processing of these metals. Tantalum and molybdenum lend themselves to the ordinary machine-shop operations. Tungsten gives difficulty with machine tools, apparently, more because of a property resembling toughness than hardness; it is quite readily filed and ground. Tungsten, at high temperatures, has a much greater rigidity than the other two. Molybdenum and tantalum, when heated very hot, recrystallize, become soft, pliable, and non-elastic while tungsten has an elasticity somewhat resembling that of a quartz fiber.

Uses of Tungsten

Tungsten is used as filament material in incandescent lamps, radio tubes, x-ray tubes, rectifying valves, and similar apparatus. It is also used as internal structural material in these devices. Here it has some limitation because of difficulty in shaping and working, especially when cold. Special glasses are produced with a coefficient of expansion similar to that of tungsten and the metal has a rather wide use for making vacuum seals through glass. The high melting point, high density, and

low volatility make it valuable as anticathode material in x-ray tubes Under some conditions, it is valuable as a resistance element in high-temperature electric furnaces.

Tungsten is universally used for contact points in the distributor of automobile-battery ignition systems. It has proved useful as a contact in many devices where the current and voltage are relatively low, such as magnetos, thermostats, speed-regulating devices, relays, etc. In its use in automobile ignition devices, it does not usually serve simply to substitute tungsten for some material that has been previously used, for instance, platinum. The action of these two metals as contacts is quite radically different and the electrical characteristics of a device that has been balanced for platinum may make it quite unsatisfactory for use with tungsten and vice versa. The basic difference of these two metals in contacts appears to be due to the fact that platinum does not oxidize and there is always a metal-to-metal contact. In the case of tungsten, however, the make and break of a circuit are accompanied by some oxidation. It is necessary that the characteristics of the circuit be such that this oxidation is controlled in such a manner that too high a contact resistance is not set up. A recent investigation indicates that if tungsten contacts are operated in a neutral atmosphere, such as hydrogen, their operation in a given device is similar to that of platinum in air. In hydrogen, there is no corrosion of tungsten and its usual peculiarities, resulting from the formation of oxide in air, are absent. In the production of contacts for automobile work, it is usual to saw the tungsten disk from a rod: The working of the tungsten rod is carried out below the temperature of equiaxing. The resultant contact surface, therefore, has the end or the smaller cross-sectional area of the crystals exposed. However, a large number of contacts are also made from disks punched from sheet. In this case the larger longitudinal sections of the crystals are exposed.

Various electrical-discharge apparatus utilize tungsten as spark-gap electrodes. Here, again, its high melting point and low volatility make it applicable.

Uses of Molybdenum

The relative ease of handling and shaping molybdenum in the cold state makes it applicable to a number of uses where tungsten is not perfectly suitable. Broadly speaking, however, it may be put to uses similar to those of tungsten. Molybdenum has been found useful as electrical contact points in cases where conditions were not so severe as to demand tungsten and where the relative ease of riveting and spinning permits its use in a more limited space.

Molybdenum would doubtless have extensive uses for making vacuum seals in glass, provided there was available a low melting glass of proper

temperature coefficient of expansion. Molybdenum is used as a filament material in devices similar to those in which tungsten is used. It has been found quite satisfactory as a filament in radio and other rectifying uses, where the requirements are such that it is not forced to operate at too high a temperature. At temperatures much above white heat, the relatively high volatility and low tensile strength of molybdenum limit its uses.

As structural and electrode elements in electronic tubes, molybdenum is widely used. The ease of mechanical shaping, the ease with which it

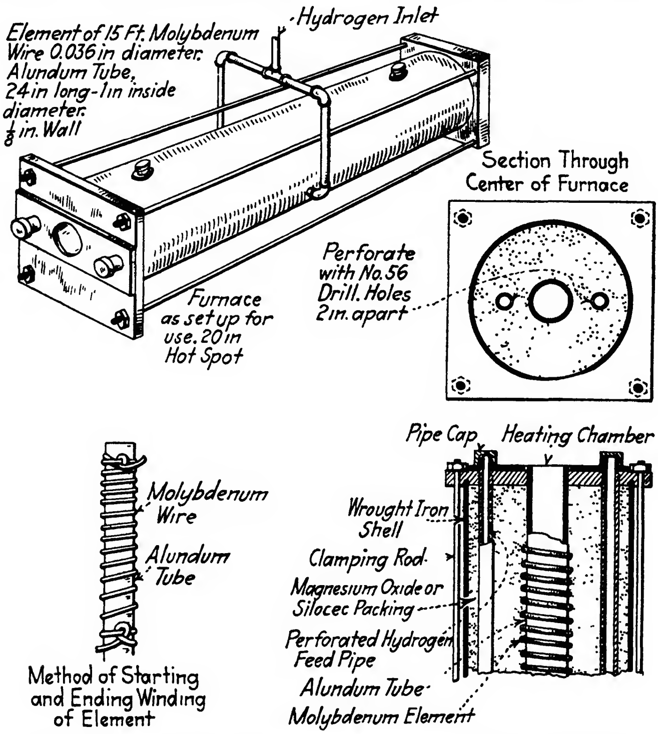

FIG. 1.—TYPICAL HIGH-TEMPERATURE ELECTRIC FURNACE.

is permanently degassed and its ability to stand high temperatures render it of special value in power tubes. "Dead soft" molybdenum wire, such as is used for grids in the radio tubes, is furnished with cold elongation up to 33 per cent.

Resistor furnaces are made by winding molybdenum on suitable refractory materials. Temperatures up to 2000° C. may be obtained. It is necessary that a neutral atmosphere be kept around the winding while it is hot; for this purpose hydrogen or nitrogen are most often used. The construction of a high-temperature furnace, using molybdenum wire as a resistor heating material, is shown in Fig. 1. A tem-

perature up to 1700° C. may be obtained in this furnace. With a suitable refractory a temperature approximating 2500° C. could be reached. The use of hydrogen is necessary to preserve the molybdenum from oxidation. Before turning on the current, enough hydrogen should be allowed to flow into the outer shell to displace the oxygen. After this a small stream of hydrogen is sufficient to protect the heating element.

The refractory should be sufficiently porous to permit the escape of hydrogen into the tube. Zirkite is a more satisfactory packing than sand or silocel, as the latter attack the molybdenum at high temperatures.

If care is taken to protect the molybdenum winding when the furnace is above 350° C., its life should be more than 500 hr. at 1400° to 1600°. Failure is usually due to deformation or melting down of the refractory or the packing.

Uses of Tantalum

Metallic tantalum first became an article of commerce about 1904, when it was used as a lamp filament by Siemens & Halske, Charlottenberg, Germany. Between 1905 and 1911, it is estimated that over 100,000,000 tantalum-filament lamps were used in this country; some of them are still in service. The writer's attention was called to one of these lamps that was still in service in the fall of 1924, which had been installed 15 years ago.

The standard lamp with 25 Hefner candlepower of 1½ watts per candlepower consumption used a filament 650 mm. long and 0.05 mm. (0.002 in.) diameter, weighing 0.022 gm.; 1 kg. of wire produced about 45,000 lamps. At the temperature of incandescence, the resistance of filaments 1 meter long and 1 mm. cross-section is 0.830 ohms. Some characteristics given for tantalum lamps are as follows:

Watts per Hefner candlepower	1.6
Hefner candlepower per square millimeter of surface	0.307
Temperature of incandescence	1700° C.
Ratio of hot to cold resistance	6.07

In 1909, the tungsten-filament lamp began to displace the tantalum lamp and within a few years the tantalum lamp became practically obsolete. There is, at present, some renewed interest in the further possibilities of tantalum as a lamp-filament material. Its high resistance and lack of brittleness after use should render it of value in cases where difficulty is encountered with tungsten.

Tantalum is of special value as structural and electrode elements in electron vacuum tubes. Its physical properties, including its high melting point, susceptibility of being made in widely varying degrees of elasticity and pliability, and its resistance to structural change at relatively high temperatures make it quite adaptable. Its physico-chemical property of absorbing and holding gases renders it quite effec-

tual as a clean-up medium, or "getter" in hard or gas-free tubes or in tubes in which it is particularly desirable to get rid of some particular gas contained. For such purposes, it is customary to weld or rivet a small piece of tantalum to the plate of the tube or to some structural parts that become heated during the process of evacuation. It would doubtless be of advantage to make the entire plate, grid, and supporting structure of this metal. The present cost, however, precludes this in any but the most exacting cases. Its use as a structural material in tubes appears to be more general in Europe than in this country. Tantalum is exported from this country for this purpose.

Tantalum is useful, also, as a filament material in vacuum tubes. Some precautions must, however, be observed in its use which are not necessary in the case of tungsten and molybdenum filaments. The absorption of a slight residue of gas may change its electrical properties quite markedly. Absorbed gas may generally be removed by heating to incandescence; it will, however, be reabsorbed by the cooling metal unless it has meanwhile been pumped out or otherwise eliminated.

Tantalum has been used for dental instruments and surgical tools; it has been largely superseded by such materials as stellite and the more recently developed non-corroding steels.

Its great resistance to wet chemical corrosion, it being attacked by no mineral acid except hydrofluoric, suggests its use for laboratory and industrial chemical and electrochemical purposes. Sheets of tantalum were partly immersed in the following solutions without gain or loss in weight at the end of 50 days: Concentrated sulfuric acid, dilute sulfuric acid, concentrated hydrochloric acid, dilute hydrochloric acid, aqua regia, glacial acetic acid, 10 per cent. acetic acid, 50 per cent. formic acid, 12 per cent. formic acid, 10 per cent. oxalic acid, 85 per cent. phosphoric acid, 10 per cent. phosphoric acid, 5 per cent. carbolic acid, 15 per cent. tannic acid, 20 per cent. sodium acetate solution, 10 per cent. iodine solution, citric acid solution, 10 per cent. potassium hydroxide solution.

The pieces were so placed that a portion was immersed and a portion exposed to atmosphere above the liquid, it having been observed that the greatest corrosion often takes place at the junction of metal, liquid, and atmosphere.

In a similar test in which the sheet was immersed in 33 per cent. potassium hydroxide solution for 120 days, the metal showed a discoloration but there was practically no change in weight.

Tantalum appears adaptable to a wide variety of laboratory uses where it is not subjected to heat; dishes, spatulas, spoons, electrodes for electroanalysis and other purposes can be made of the metal.

The Tantalum Electrolytic Valve

It has been known since early in the twentieth century that many metals have properties as a result of which they may be described as electrolytic valves. When two different metals or conductors are made the electrodes in an ionized solution, there is often considerable difference in the ease with which current will flow from one with reference to the other. An electrolytic cell, with one electrode of aluminum and one of steel in an electrolyte of boric-acid solution, for instance, is known as the Nodon electrolytic valve. If a current potential is placed on the electrodes of this cell, current will pass with relative ease in the solution from iron to aluminum but much greater resistance is offered to its passage from aluminum to iron in the solution. That is to say, aluminum will give off electrons to the solution to free positive ions in the solution but will not readily absorb them to free negative ions. Magnesium, cadmium zinc, bismuth, and antimony are some of the other metals showing rather marked valve action. The resistance of these metals to chemical corrosion is low, however, and, except in the case of aluminum, but little has been done to make practical use of this interesting property.

Tantalum is highly resistant to both chemical and electrolytic corrosion and very strikingly to corrosion of the strong mineral acids. It is also an electrolytic valve metal. This combination of properties has recently led to its commercial use in rectifiers and battery chargers for converting alternating current into direct.[1] If two plates of tantalum are immersed in a suitable electrolyte, for example dilute sulfuric acid, and if these plates are connected to a source of alternating-current supply, current will flow for a few seconds during which time a thin film is formed on the surface of the plate. This film may show play in colors, while it is forming, similar to a piece of steel that is being heated to its bluing temperature. At the end of a few seconds, current no longer flows, provided the impressed voltage is not too high. If, instead of using two tantalum plates, one plate of tantalum and one of, say, lead is used, and if instead of an alternating-current potential we impress direct current so that there is a tendency of current to flow from tantalum to lead in the solution, which means that electrons will tend to flow from solution to tantalum, an effect similar to the above takes place on the tantalum and current flow ceases shortly, provided again the impressed voltage has not become too high. If this same cell is connected to a source of direct-current potential, the polarity being such that the current inside the cell tends to flow from lead to tantalum, current passes quite readily.

[1] U. S. Patent 1495582.

Finally, if the cell with an electrode of tantalum and one of lead and dilute sulfuric-acid electrolyte is connected to a source of alternating current, one-half of the alternating-current wave will be suppressed, the one whose time interval tends to send current from tantalum to lead. During the other half of the wave, current passes from lead to tantalum. The net current flow is pulsating unidirectional. This current is in effect direct and may be used to charge batteries, electroplate, perform electrolysis, and do much of the work for which direct current is required. If a steady non-pulsating direct current is required, the pulsating current may be smoothed by means of an electrical filter system. In this electrical filter system, it is practical to use electrolytic electrical condensers containing tantalum as electrode material.

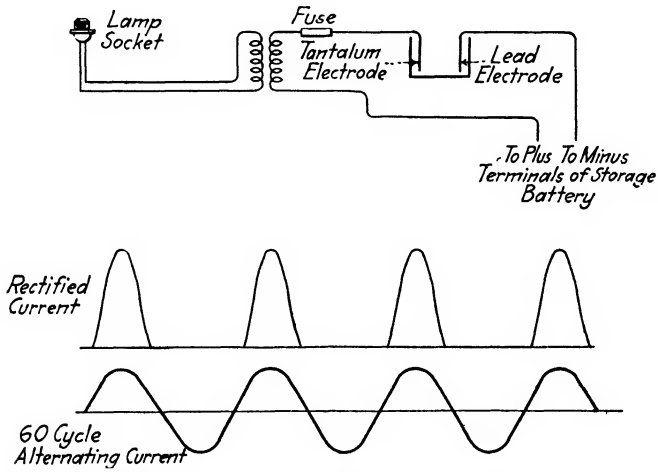

FIG. 2.—RECTIFIER USING ONE-HALF OF ALTERNATING-CURRENT WAVE.

Commercial cells are now available for direct-current output up to several amperes. Where high-voltage output is required, several cells are used in series. The maximum alternating-current voltage recommended to be impressed per cell for constant service is 40. Units consisting of transformer, cell, and output control are available for battery charging, either continuous or intermittent, electroplating, electrolysis, direct-current supply for radio operation, and various applications where a small supply of direct current is required. A diagrammatic sketch of such a rectifier is shown in Fig. 2.

Similar rectifiers that utilize both halves of the alternating-current wave are also manufactured. This is accomplished by using two cells or series of cells or by using a single cell with two tantalum electrodes. Fig. 3 shows the electrical connections of such a rectifier.

The economical use of the tantalum rectifier is limited to installations of relative small wattage outputs. Conversion from alternating

to direct current is accompanied by considerable loss of energy, which is largely dissipated as heat in the cell. The passage of the current through the cell results in liberation of hydrogen from the tantalum electrodes and oxygen at the lead; water must be added from time to time to replace this decomposition.

A interesting and valuable effect is obtained in a rectifier cell by adding to the sulfuric-acid electrolyte, a salt of a metal readily reduced by wet electrolysis, such as iron, nickel, copper, silver, etc.; this acts as a depolarizer and greatly decreases the internal resistance of the cell. The effect is so marked that in the charging of a battery, for instance, the current output of a rectifier cell may be multiplied several times, the alternating-current voltage remaining constant, by the addition of such a salt. Similarly, a given output in amperage may be obtained

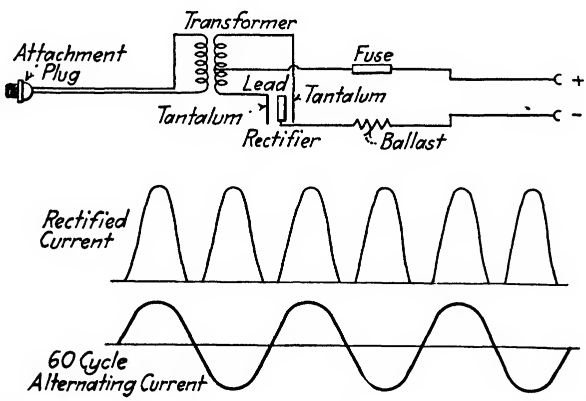

FIG. 3.—RECTIFIER USING BOTH HALVES OF ALTERNATING-CURRENT WAVE.

at a much less impressed alternating current when a depolarizing salt is used. The depolarizer is also valuable for stabilizing the operation of the cell and rendering the valve electrode less subject to ill effect from abuse. The depolarizer appears to act by cutting down the resistance of the cell at or near the surface of the rectifying electrodes. It is believed to be, in some way, coupled with the effect that a relatively non-insulating metal film is produced as primary product of electrolysis instead of a gas film where depolarizer is not added. A further study of this depolarizing property will doubtless lead to more definite interesting details of its mechanism.

The current output of a rectifier cell is limited by the current that may be obtained without overheating the electrolyte. While rectification will continue even in a boiling solution, the practical upper limit of electrolyte temperature may be regarded as around 70° C. Temperatures above this are likely to result in excessive evaporation, annoying odors, and softening of rubber parts, if such are used in the cell assembly.

Larger current output from a system may be had by connecting two or more cells in such a manner that both halves of the alternating-current wave are rectified or by connecting cells in parallel. Where higher voltage output is desired, it is necessary to connect cells in series, as above mentioned. For installations used for charging batteries where there is a back electromotive force, the fact must be remembered that when an electrode is acting as a closed valve it is not only blocking the alternating-current potential but this potential to which the battery voltage is added.

In a study of current rectification the action of a large number of electrolytes has been observed. Considered from all standpoints where the high current output is desired, sulfuric acid of a gravity of 1.100 to 1.250, which is the same approximately as is used in lead-type storage batteries, to which has been added ferrous sulfate crystals (not more than 1 gm. to 100 c.c. of solution) has thus far proved the most satisfactory.

In one series of electrolyte tests, 2 per cent. solution of sodium carbonate, 2 per cent. solution of sodium pyrophosphate, 1 per cent. solution of sodium chloride, 4 per cent. solution of sodium acetate, 2 per cent. solution of potassium bisulfate, 2 per cent. solution of nitric acid, 5 per cent. solution of sodium tungstate, 4 per cent. solution of sodium sulfate, 2 per cent. solution of sodium fluoride, and 2 per cent. solution of sodium bicarbonate showed but little current leakage. A 2 per cent. solution of ammonium phosphate showed appreciable leakage, 10 per cent. solution of acetic acid and 2 per cent. solution of ammonium tungstate showed a great deal of leakage, the acetic-acid solution exhibiting hardly any valve action. Considerable experience in the design of tantalum rectifier apparatus has, however, shown that current leakage is not the only criterion of a good rectifier, although it is an important one. Some electrolytes, it has been found, result in undue heating; others dissolve one or more of the electrodes and still others may embrittle the electrodes without actually dissolving. A great deal of further investigative work on the rectifying action of tantalum is in progress in the laboratory of this company and it is hoped that a comprehensive report of the work may be presented at an early date.

Metallography of Tantalum

Preparation of Specimens

Though apparently a very soft metal, tantalum is cut with difficulty with a hack saw. An unusual amount of heat is liberated when an attempt is made to saw the metal and the teeth of the saw are softened after a few strokes. In certain specimens, extremely hard metallographic inclusions are present, which make sawing even more difficult. The

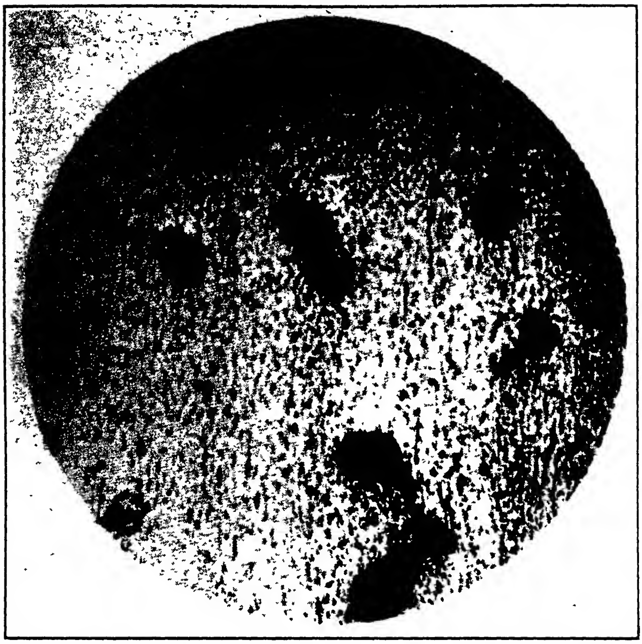

FIG. 4.—TANTALUM, UNETCHED, SHOWING PITS. × 600.

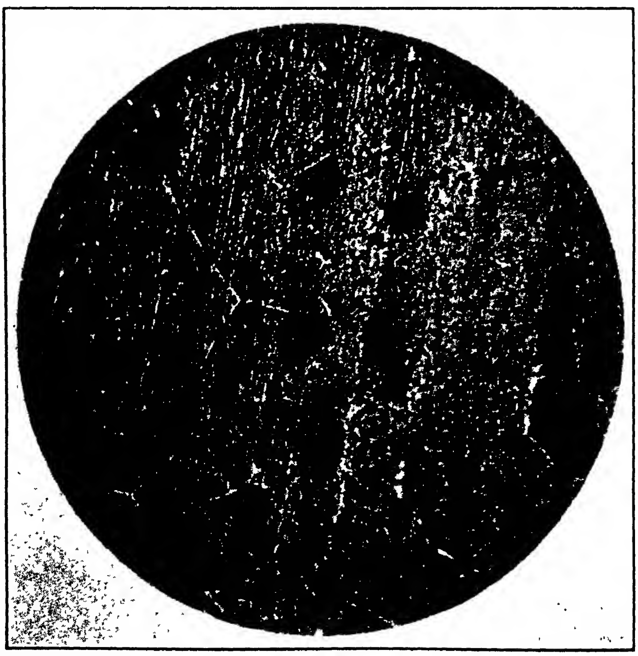

FIG. 5.—TANTALUM, UNETCHED, SHOWING PITS AND THREADS OF CARBIDE. × 600.

metal drills with some difficulty, but works fairly well on the lathe. The usual method of cutting it is with a carborundum disk.

Polished sections for metallographic examination may be prepared by filing to a flat surface, smoothing down with No. 1, 0, 00, and 000 Manning polishing papers, and finally polishing on a wheel covered with pool cloth using levigated alumina. The surface thus produced is not all that could be desired but has been satisfactory. A little study of the polishing materials and methods might lead to much better results.

The grain structure of the metal can be brought out by cold H_2F_2 contained in a platinum dish. Contact between the tantalum and platinum seems to have a beneficial effect upon the reaction. Following the etching, the specimen should be washed with hot water. Unless H_2F_2 is completely removed, there is danger of ruining the microscope lenses.

Structure of Pure Tantalum

Unetched specimens appear homogeneous and without structure. Some specimens of apparently pure metal seemed to show an abnormal tendency to develop holes when they were polished; this may have been caused by prolonged polishing or it may have been that the specimens contained voids, which were enlarged by the polishing material; see Figs. 4 and 5.

Etched sections of metal that has received considerable mechanical work interspersed by heat treatments show a well-defined grain structure. The polyhedral shape of the grains is unusually perfect and the boundaries are straight rather than curved lines. The size of the grains is somewhat larger than that of the ordinary run of sintered tungsten; see Fig. 6.

Corbon in Tantalum

When unetched sections from certain tantalum samples are examined under the microscope, an obviously hard constituent appears in relief at the grain boundaries and, occasionally, within the grains. By correlating the amount of this constituent, as seen under the microscope, with the amount of carbon present, as determined by analysis, this material has been proved to be tantalum carbide. The constituent appears whenever the carbon runs above 0.05 or 0.06 per cent. (see Fig. 7) and occurs in masses when the carbon is 0.75 per cent. as shown in Fig. 8. Whether tantalum has the property of dissolving carbon up to 0.05 per cent., and what the effect of such dissolved carbon would be on the properties of the metal has not been determined. A number of specimens showing traces of carbon by chemical analysis showed no indication of it microscopically. A bar that, by accident, came in contact with some rubber when it was hot had a coating of

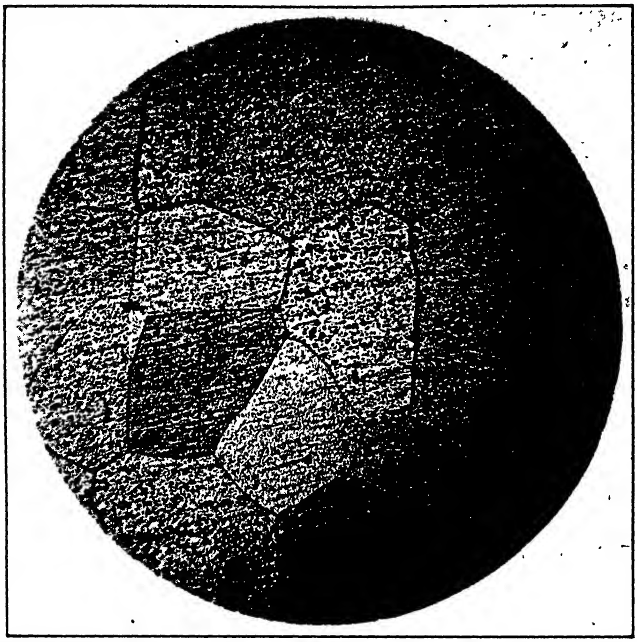

FIG. 6.—TANTALUM, ETCHED, SHOWING POLYHEDRAL STRUCTURE OF PURE ANNEALED METAL. × 300.

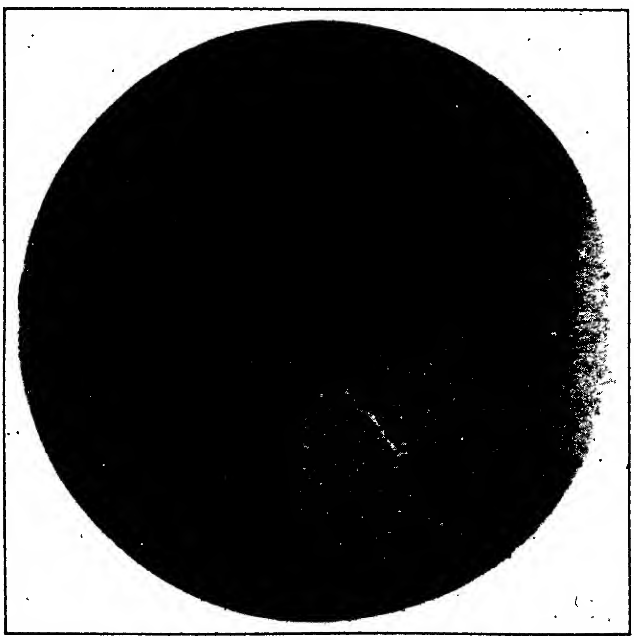

FIG. 7.—TANTALUM, CONTAINING ABOUT 0.06 PER CENT. CARBON, UNETCHED. × 600.

Fig. 8.—Tantalum with high carbon content, unetched. × 600

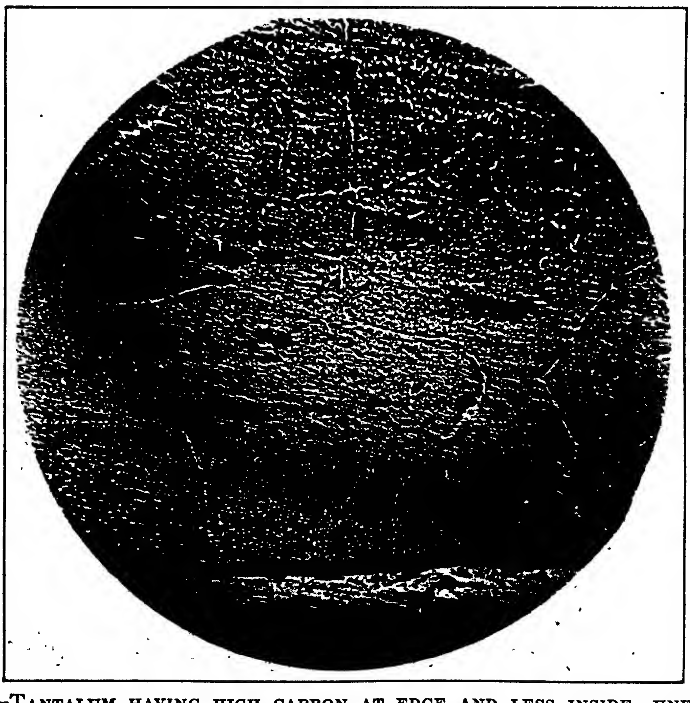

Fig. 9.—Tantalum having high carbon at edge and less inside, unetched. × 300.

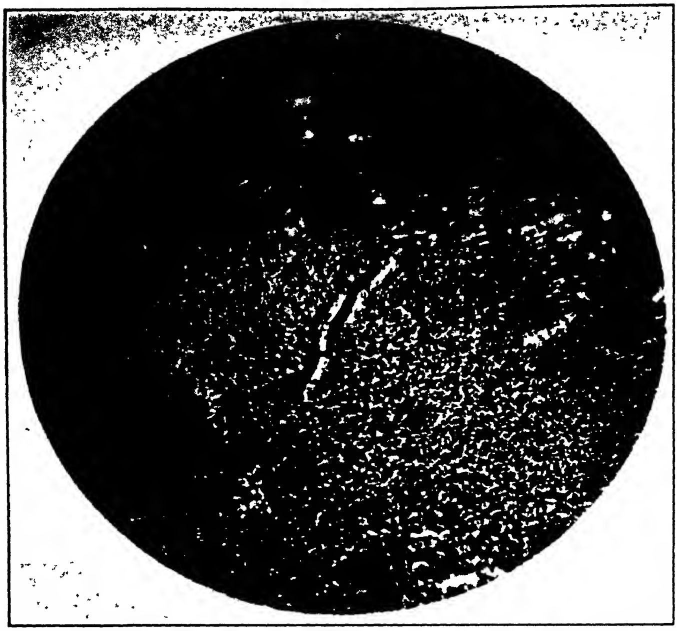

FIG. 10.—PATH OF FRACTURE FOLLOWING CARBIDE, UNETCHED. × 1000.

FIG. 11.—TANTALUM BRITTLE DUE TO ABSORBED HYDROGEN, ETCHED. ×

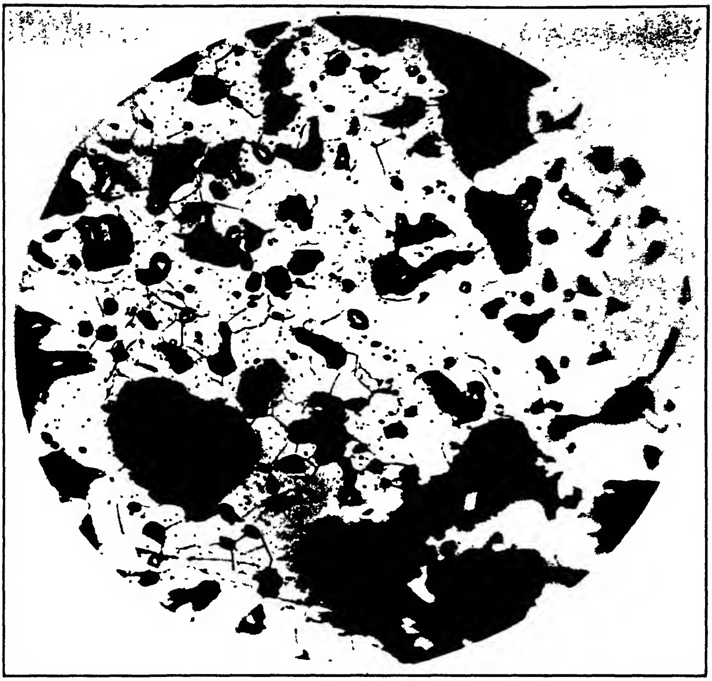

Fig. 12.—Tantalum brittle from heating in air, probably from absorbed nitrogen; etched. × 300.

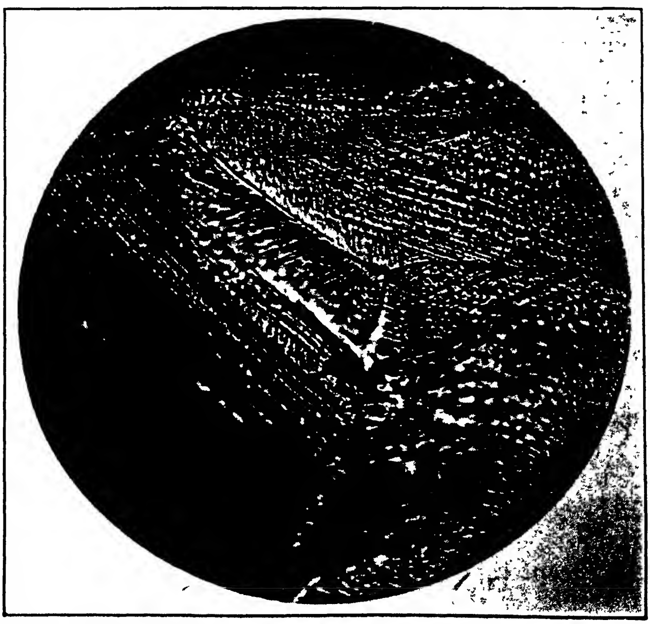

Fig. 13.—Slip bands in strained specimen.

carbide of considerable thickness on the outside and a smaller amount had diffused some distance into the bar; see Fig. 9. The center of the bar was almost free from carbide.

The effect of this carbide on the working properties of the tantalum is about what would be expected when its hard, brittle nature is considered. Bars that show traces of carbide under the microscope roll well. When enough carbon is present to begin to outline the grain boundaries, the metal will roll into sheets but the sheets will be brittle both parallel and at right angles to the direction of rolling, and there is a tendency for seams to show on the surface. When any large amounts of carbide are present, the metal cracks badly after a very little rolling.

In an effort to show the brittle nature of this carbide, a specimen that contained considerable amounts of it was polished and then stressed until it cracked The path of fracture followed the carbide wherever there was an opportunity. Fig. 10 shows a case where a crack can be clearly seen to originate in a carbide particle.

Absorption of Hydrogen, Nitrogen, and Oxygen

When a tantalum bar is heated and cooled in hydrogen, it is exceedingly hard on the outside. Only a very unsatisfactory section can be prepared, but when such a section is etched it shows a definite polyhedral structure; see Fig. 11. This indicates that hydrogen forms a solid solution with tantalum. The outside, which is in direct contact with a hydrogen atmosphere, dissolves a large amount of it as the bar cools down and becomes very hard and brittle.

Nitrogen also seems to dissolve in tantalum in much the same way. The examination of an etched section of a bar, to which air was admitted when it was hot, showed a regular polyhedral structure; see Fig. 12. The bar was exceedingly hard. It has been assumed that the hardness of tantalum that has been heated in air is due to nitride formation or, according to our observations, a solution of nitrogen in tantalum. Though there is no definite proof that part or all of this hardening is not due to oxygen, it is not probable.

As microscopic examination indicates that nitrogen and hydrogen, when present in tantalum, are held in solid solution and as it is a general observation that an impurity held in solid solution in a metal hardens it in direct proportion to the amount present, it follows that small amounts of these gasses will have a hardening effect on the metal. This may explain the observation that some metal rolls without cracking, but seems to be unusually hard.

Fig. 13 shows an etched surface of tantalum that has been severely strained. The slip bands produced are much like those observed in other metals except that they may be closer together.

The Malleability of Nickel*

By Paul D. Merica,† Ph. D., New York, N. Y., and R. G. Waltenberg,‡ Bayonne, N. J.

(New York Meeting, February, 1925)

Although nickel was discovered and isolated as early as 1750 and its valuable properties recognized, many years passed before it was used commercially for wire, sheet, rods, etc., in the pure form. This was due partly to its high cost at that time and partly to the fact that it was not possible to refine and cast nickel into ingots sufficiently malleable to be amenable to the usual forging, rolling, or drawing processes. So remarkable was this fact, and so different from the experience at that time with metals such as copper and iron, that it has left its impress on the nomenclature within the nickel industry. To this day, furnace-cast nickel produced in such a manner as to be suitable for rolling and forging is called *malleable nickel* to distinguish it from the ordinary pig and shot nickel of commerce.

In 1878, the firm of Jos. Wharton, of Philadelphia (which later became The American Nickel Works, a constituent of The International Nickel Co.) exhibited at the Paris Exhibition specimens of rolled pure nickel strip and of drawn nickel wire. About this time, there was considerable activity in the study of the refining of nickel and several methods were described, some of which were patented, for the production of furnace-cast malleable nickel including the use of manganese (Boeddicker,[1] Selve and Lotter[2]), the use of potassium permanganate (Bernsdorfer Metallwarenfabrik[3]) and the use of phosphorus (Garnier[4]). By far the most efficient method was discovered by Th. Fleitmann in 1879;[5] it consisted in adding to the molten nickel, just before pouring the castings, from 0.05 to 0.125 per cent. of metallic magnesium. This soon became the recognized final malleableizing treatment for furnace-cast nickel.

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† Director of Research, The International Nickel Co.

‡ Research Metallurgist, The International Nickel Co.

[1] Wiggin Process for Production of Malleable Nickel. Wagner's Jaresberichte (1881) **27**, 69.

[2] Production of Nickel Free from Oxide. German patent 25798 (1883).

[3] German patent 28989 (1884).

[4] On a New Process of Obtaining Malleable Nickel. C. R. (1880) **91**, 331.

[5] *Ber. d. deutsch Gesell.* (1879) **12**, 454.

It is evident that the use of these elements was based on the thought that they would reduce and eliminate nickel oxide, which was presumed to be the direct cause of the brittleness of ordinary furnace-cast nickel. Fleitmann, however, did not speak of his magnesium treatment as designed to eliminate nickel oxide but believed that it removed either carbon monoxide (by its reduction to carbon) or cyanogen compounds. He later refers to the use of manganese to flux, and to removed sulfur,[6] anticipating in a general manner our own conclusions.

Today, even with modern methods of refining and improved furnace practice, nickel castings are not, in general, malleable without the magnesium treatment; and after 45 years the Fleitmann method, somewhat modified, it is true, is used exclusively for the treatment of nickel intended for malleable castings, as well as for the treatment of many nickel-bearing alloys, such as monel metal, etc. It is customary today to produce malleable nickel with a manganese content of at least 0.10 per cent. and to add, as a final refining treatment of the molten nickel, about 0.1 per cent. of metallic magnesium.

The Fleitmann method has been so successful that, since the early days of its discovery and of the experimentation with manganese and other elements, little consideration has been given to the mechanism of its effect; the operation has been and still is referred to as "deoxidation," sometimes "degasification." In recent years, a number of phenomena have served to focus attention again upon this question and it has become increasingly evident that there was something else in the action of magnesium on nickel and its alloys than deoxidation or degasification.

The investigation here reported was taken up in the summer of 1921 with the specific purpose of ascertaining: (1) why ordinary cast nickel is not malleable, when not treated with magnesium, and (2) what is the mechanism by which the magnesium treatment produces malleability in such nickel. Such an investigation has, of necessity, embraced a considerable study of the metallography[7] of nickel and some of its alloys, and has brought to light some interesting facts only indirectly related to the principal themes. Of these, perhaps the most interesting are the results of the study of the equilibrium between nickel and nickel oxide.

Why Nickel is Non-malleable

Commercial cathode, or electrolytic, nickel of high purity[8] is itself malleable and its malleability is not destroyed if such nickel is melted

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[6] German patent 28460 (1884).

[7] The metallography of nickel and its alloys has been the subject of a number of valuable investigations, but it is unnecessary to mention all here. A discussion and bibliography of these investigations is given in Bureau of Standards Circular 100 on Nickel; we should like to refer also to Physical Properties of Nickel, by D. H. Browne and John F. Thompson, *Trans.* (1920) **64**, 387; which deals particularly with the metallography of nickel containing small amounts of the usual commercial impurities.

[8] Containing about 0.4 per cent. cobalt, 0.1 per cent. iron, 0.02 per cent. copper.

in a crucible with ordinary precautions to prevent the absorption by it of impurities. Small ingots of electrolytic nickel melted and cast in this manner, without treatment of any kind, may be readily forged under the hammer both hot and cold without cracking. Evidently lack of malleability is not an inherent property of nickel.

A series of small laboratory melts were made of electrolytic nickel to which various impurities were added in known amounts, there being no other treatment given by magnesium or otherwise. These melts were made in an ordinary gas-fired furnace, in the Arsem vacuum electric furnace, and in the Ajax-Northrup high-frequency induction furnace, the melts varying from 200 to 3000 gm. in weight. The ingots produced from these melts were tested for malleability by hammering, both hot (1100° C.) and cold, to a thin wedge. If this could be done without cracking, the ingot was called malleable; otherwise it was non-malleable.

The principal conclusion reached from the results of these tests was an unexpected one. Of all of the impurities known to be present in furnace-refined nickel only sulfur rendered pure electrolytic nickel non-malleable—that is, of course, when added in amounts not greatly exceeding the usual ones. As long as the sulfur content of the electrolytic nickel ingot was well below 0.005 per cent. the ingot was malleable. Whenever it reached or exceeded that amount, the ingot became non-malleable and its quality was impaired in proportion to the amount of sulfur present.

The addition of such elements as carbon, silicon, iron, copper, arsenic, cobalt, manganese, and, to our surprise, oxygen did not impair the malleability, either hot or cold, of the remelted electrolytic nickel ingots. Nor did drastic exposure of such nickel to the action of carbon monoxide, carbon dioxide, hydrogen, or air affect the malleability of the nickel, except in so far as the presence of blowholes in the resulting ingot in some cases produced slivers and splits.

The experiments were sufficiently extensive, in our opinion, to allow of but one conclusion: that the lack of malleability of ordinary furnace-refined nickel is due solely to the presence of sulfur in excess of the safe limit—less than 0.005 per cent.[9] This was demonstrated to be true in similar manner for monel metal (containing about 67 per cent nickel and 28 per cent. copper) and it is suspected that it is characteristic of nickel alloys, at least those of higher nickel content.

[9] After the completion of this work, B. Bogitch (C. R. (1924) **178,** 855), states that 0.005 per cent. sulfur makes nickel cubes or rondelles non-malleable, whereas they are malleable when the sulfur content is lower. These statements confirm the conclusions of this article.

Structural Form of Sulfur in Nickel

The reason for this effect of even small amounts of sulfur on the malleability of nickel is not far to seek. Bornemann,[10] Hayward,[11] and others, have studied the equilibrium of nickel and sulfur and have shown that sulfur forms a compound, Ni_3S_2, with nickel that forms a eutectic with nickel at 21.5 per cent. sulfur, melting at 644° C.

We have confirmed these facts and have been able to identify free Ni_3S_2 in nickel microscopically when as little as 0.005 per cent. of sulfur is present, which must therefore be somewhat greater than the limit of

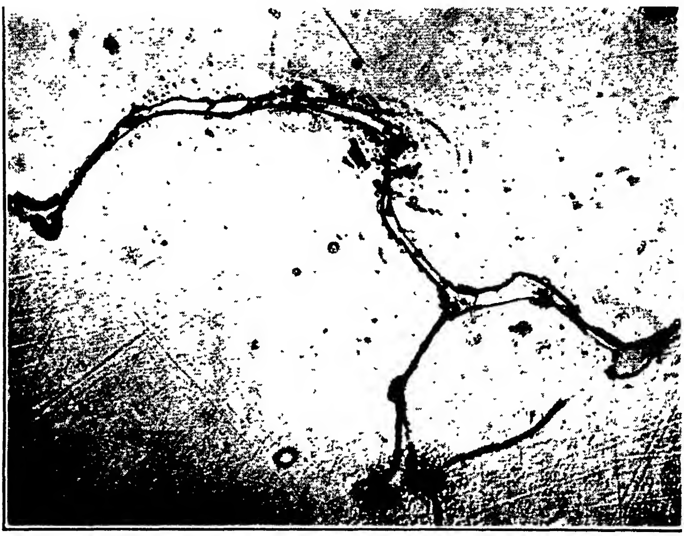

Fig. 1.—Nickel containing 0.23 per cent. sulfur; nickel-sulfide constituent is apparent at grain boundaries. × 500.

solid solubility of this compound. By thermal analysis, it was not possible to detect the eutectic arrest at about 640° C. unless about 0.03 per cent. of sulfur is present as Ni_3S_2. This compound, when present in small amounts in cast nickel, assumes the form of films surrounding partly or completely the individual grains of nickel. It has a characteristic yellowish color and is readily identified under the microscope. Fig. 1 shows the typical appearance of the Ni_3S_2 eutectic films surrounding the nickel grains. Whenever these films are present, the nickel is brittle both hot and cold. At temperatures above 650° C., the grains of nickel have practically no intercrystalline adhesion as they are separated, partly at least, by a liquid film. Below this temperature, the Ni_3S_2 film is solid but quite weak and brittle. In consequence, the fracture of

[10] *Metallurgie* (1908) **5**, 13; (1910) **7**, 667.

[11] The Equilibrium Diagram of the System Cu_2S-Ni_3S_2. *Trans.* (1914) **48**, 141.

ordinary non-malleable furnace nickel is intercrystalline both hot and cold.

Effect of Manganese and of Magnesium

Having ascertained the cause of non-malleability in nickel, it remained to study, in the light of these facts, the restoration of malleability by manganese and magnesium additions. Additional laboratory melts of nickel were, therefore, made in the same manner with various additions of sulfur, followed by successive additions of manganese and of magnesium. The typical procedure was to make a melt with over 0.005 per cent. sulfur from which one ingot was poured; thereupon a

Fig. 2.—Specimen shown in Fig. 1 treated with 3 per cent. manganese; manganese-sulfide constituent appears as a eutectic network around the grains of nickel. × 500.

small amount of manganese was added to the remainder, and a second ingot poured; finally magnesium was added and the third and last ingot poured.

These tests demonstrated that the malleability of nickel that had been impaired by sulfur additions was considerably improved by the addition of manganese and was completely restored by the addition of magnesium. This was true even of nickel to which unusually large amounts of sulfur had been added—as much as 0.25 per cent., which is over ten times the amount of sulfur generally present in commercial furnace-refined nickel.

By thermal analysis, by microscopic observations, as well as by direct chemical analysis, it was demonstrated that both manganese and magnesium, when added to molten nickel containing sulfur, react with the

sulfur to form manganese and magnesium sulfides respectively, probably MnS and MgS.

The manganese sulfide forms a eutectic with nickel melting at 1325° C., and its distribution in the solid nickel, although along the grain boundaries, takes the form of small globules and not films, as does nickel sulfide. Its deleterious effect on the grain cohesion is not so great as that of the latter. In consequence, the addition of manganese improves the malleability of nickel but does not restore it completely.

Magnesium has a higher affinity for sulfur than either nickel or manganese and reacts apparently almost quantitatively with either manganese or nickel sulfide to form magnesium sulfide. The latter is insoluble in molten nickel and, indeed, is solid at these temperatures,

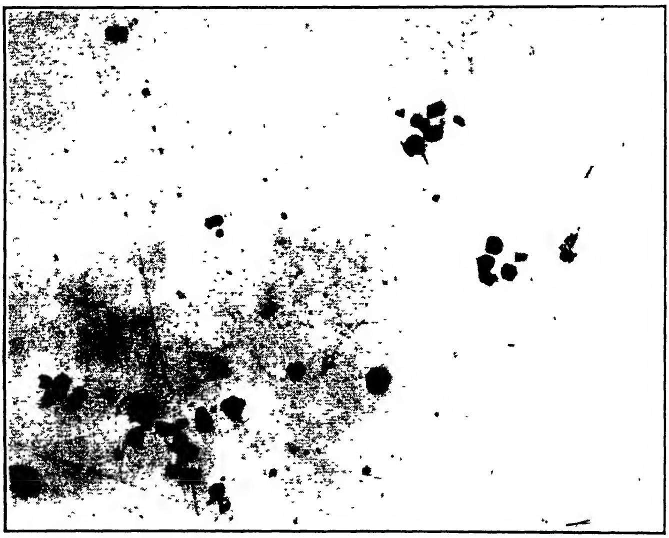

FIG. 3.—SPECIMEN SHOWN IN FIG. 2 TREATED WITH 0.5 PER CENT. MAGNESIUM; MAGNESIUM SULFIDE APPEARS AS HEXAGONAL INCLUSIONS IN THE GRAINS OF NICKEL, MAGNESIUM-NICKEL IS BARELY VISIBLE × 500.

forming small crystalline particles that are entrapped during the solidification of the nickel and dispersed throughout the grains. They are not concentrated at the grain boundaries and exert practically no effect in consequence of their uniform mode of distribution on the cohesion or malleability of the nickel.

Magnesium additions, therefore, restore the ductility of cast nickel containing sulfur, by changing the form of the sulfur from Ni_3S_2 to MgS and its distribution from that of intercrystalline films of Ni_3S_2 (of low melting point) to that of uniformly dispersed equiaxed particles of MgS (of high melting point). Figs. 2 and 3 show the typical structures of nickel containing sulfur that has been treated with manganese and with

manganese and magnesium, respectively. It is worth while to point out that MgS is attacked by water, so that to prepare a metallographic specimen containing it alcohol must be used in the final polishing, otherwise only pits will be left as the evidence of the presence of MgS.

Although the principal function of magnesium (and of manganese to a less extent) in rendering cast nickel malleable is thus demonstrated to be its effect in changing the form of the sulfur present, this is not the only rôle it plays. Magnesium undoubtedly reacts, as Fleitmann claimed, with oxides, and particularly with carbon monoxide; this serves to "degasify" the molten metal, as well. Irregularities in the effects

FIG. 4.—NICKEL-NICKEL OXIDE EUTECTIC, CONTAINS 0.24 PER CENT. OXYGEN (1.1 PER CENT. NiO); ETCHED (30 PARTS NITRIC, 30 PARTS ACETIC, 40 PARTS WATER). × 500.

produced by added magnesium may indeed be traced very probably to a varying distribution of the amount added between these two functions.

Essentially the same studies were made with monel metal and what has been said about the "malleableizing" of nickel may with equal accuracy be said about monel metal, and probably other high-nickel content alloys as well. The structural forms of sulfur, manganese, and magnesium in the alloys are somewhat different from the forms they assume in nickel but the essential features are not different. Sulfur embrittles and manganese and magnesium restore malleability.

NICKEL AND OXYGEN

Inasmuch as the equilibrium between nickel and oxygen had not previously been subjected to any detailed study, the main features of

their equilibrium were determined. Oxygen reacts with molten nickel to form apparently only one stable oxide, NiO. This oxide is soluble in molten nickel in all proportions and forms with it a simple eutectic series, the eutectic melting at 1438° C. and containing 0.24 per cent. of oxygen or 1.1 per cent. of NiO. The melting point of NiO appears to be about 1655° C. The solubility of NiO in solid nickel appears to be very slight, although this was not studied in detail.

Contrary to general belief, nickel that is free from sulfur but contains nickel oxide up to the eutectic composition is quite malleable, both hot and cold. As a demonstration of this, a 1-in. diameter ingot of the eutectic composition was forged hot to a 0.25-in. diameter bar and this bar was drawn cold, with intermediate annealing, after about 80 per cent. reduction to a satisfactory wire of 0.009-in. diameter. The microstructure of the ingot from which this wire was produced is shown in Fig. 4, which illustrates the typical structure of the nickel, nickel-oxide eutectic. It is quite similar, in general appearance, to the copper, copper-oxide eutectic.

ACKNOWLEDGMENTS

This work was carried on by Mr. Waltenberg as Research Associate of The International Nickel Co. at the Bureau of Standards and the authors desire to express their deep appreciation of the privilege of this association with the Bureau, and of the many courtesies and aid of its Director, Dr. G. K. Burgess. They are indebted as well to Messrs. H. A. Bright and J. A. Scherrer, of the Bureau, for many chemical analyses, and to Mr. E. J. Ruh, Research Assistant, for general assistance. To Mr. A. J. Wadhams, Manager of Development and Research Department of the International Nickel Co., special thanks are due for the generous and sympathetic support he has accorded this work at all times.

DISCUSSION

H. W. GILLETT,* Washington, D. C. (written discussion).—The conclusions reached in this paper, that sulfur which is not combined with some other element, such as manganese or magnesium, but is free to form nickel sulfide, is the cause of poor malleability, while over 0.20 per cent. oxygen can be present in a sulfur-free nickel without causing loss of malleability, are paralleled by the findings of Cain in regard to iron.

Cain[12] finds that when sulfur in iron is below 0.01 per cent., 0.20 per cent. oxygen can be present without red shortness. (This is corroborated by the work of Tritton and Hanson[13] at the National Physical Laboratory,

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[12] J. R. Cain: Bureau of Standards *Tech. Paper* 261 (1924).

[13] F. S. Tritton and D. Hanson: Iron and Oxygen. Iron and Steel Inst. *Preprint* (1924).

who state that iron containing 0.10 per cent. oxygen but only a trace of sulfur has considerable ductility both hot and cold.) If manganese is present in suitable amounts (three times that of sulfur) and oxygen in only normal amount, red shortness is prevented, but as oxygen increases, that ratio of manganese to sulfur must be exceeded, doubtless because much of the oxygen is combined with manganese, thus lowering the effective manganese and leaving some sulfur loose to form iron sulfide.

Wimmer[14] finds that iron with 0.04 per cent. carbon, 0.115 per cent. oxygen, 0.038 per cent. sulfur, and 0.34 per cent. manganese is not red short, while that with 0.04 per cent. carbon, 0.129 per cent. oxygen, 0.032 per cent. sulfur and 0.26 per cent. manganese is red short. The increase of 0.014 per cent. in oxygen is accompanied by a decrease of 0.12 per cent. in manganese, and the red shortness that Wimmer ascribes to oxygen would more logically be ascribed to the indirect effect of the oxygen in causing a deficiency in manganese. It seems reasonable to assume that the inclusions present in iron or steel high in oxygen and containing manganese are largely composed of some oxide of manganese. Such inclusions, as Wimmer shows, are highly deleterious to the mechanical properties, but it is quite likely that any other brand of "dirt" similarly distributed would be as bad as the oxygen. This will doubtless apply also to nickel and monel. Recent work at the Bureau of Standards has definitely connected relatively poor impact values of a certain lot of monel with an excessive amount of inclusions, and we would expect that nickel or monel high in oxide would be of poor quality, even though it is still malleable and ductile.

Feild[15] informed the Institute a year ago that zirconium combines with sulfur and prevents red-shortness, and cerium[16] has been found to exert the same effect. Under some circumstances, Cain finds that copper may perhaps act similarly, and aluminum is also credited with this power by some observers. All these observations tend to strengthen our belief in the correctness of the explanations given by Merica and Waltenberg in the case of nickel. Sulfur-binding in metals like iron and nickel is one of the important effects of what has heretofore been considered deoxidation.

Ancel St. John,* New York, N. Y.—About two years ago I used the x-ray analysis on a nickel alloy to determine why certain materials were non-malleable while others, apparently made in the same way, were forgeable. The x-ray patterns at once showed the presence of quite strong lines, due apparently to some alloy with nickel that should not

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[14] A. Wimmer: *Stahl und Eisen* (1925) **45**, 73.

[15] A. L. Feild: *Trans.* (1924) **70**, 201.

[16] H. W. Gillett and E. L. Mack: Bureau of Mines *Bull.* 199 (1922).

be there. At that time I suspected that it was a nickel-oxide-nickel alloy of some sort, but evidence produced here would indicate that it was the sulfide. I would suggest that it might be perfectly possible to get conclusive evidence along that line by preparing control specimens, in which you know whether you have sulfide or oxide as the constituent and compare the x-ray patterns.

L. W. McKeehan,* New York, N. Y.—The authors have suggested that other nickel-rich alloys may show the same effect. While I have no definite information regarding the amount of sulfur in certain nickel-iron alloys with which I have had experience, I can say that they sometimes show intercrystalline brittleness. In no case has metal prepared with the addition of magnesium in the ordinary way shown such brittleness. This may be taken, perhaps, as a confirmation of the results here reported. The amount of nickel in the alloys I dealt with was from 100 to 50 per cent. or less.

A. L. Feild,† New York, N. Y.—In the discussion of this paper, it has been stated in effect that red-shortness is eliminated in steel when the amount of manganese added is sufficient to combine with any oxygen present in addition to satisfying the theoretical requirements for the formation of manganese sulfide. As a matter of fact, it is generally observed in practical steel-making operations that, to prevent red-shortness, the percentage of manganese in the finished steel must exhibit a ratio to that of sulfur of at least 2.39 to 3.60 instead of the theoretical ratio of 1.71. Inasmuch as steel does not as a rule contain more than 0.018 per cent. total oxygen, determined by the Bureau of Standards Vacuum-tube method, the performance by manganese of its dual role is greatly impeded by some distinct reversibility of reaction. That this reversibility has to do with the efficiency of deoxidation I have elsewhere shown to be true.[17] That high-oxygen steels of very low sulfur content (0.01 per cent. or less) may be hot-worked without breaking, as recently shown by Cain[18] and by Tritton and Hanson[19] does not imply that oxygen is harmless so far as red-shortness in ordinary commercial steels is concerned. It simply proves (a) that iron sulfide, when present in sufficiently minute amount, does not cause pronounced red-shortness, even when oxygen is present in greater than usual quantity, and (b) that iron oxide, as such, does not cause red-shortness. In other words, the effect of oxygen in causing red-shortness must be due to an indirect effect, which effect is exerted only when sulfur is present above a

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[17] *Trans.* (1924) **70**, 201–17.

[18] Bureau of Standards *Tech. Paper* 261 (1924).

[19] *Iron & Coal Trades Rev.* (1924) **109**, 378–81.

certain limiting concentration. The sulfur present in the vast majority of commercial steels invariably lies well above this limiting concentration. Sulfur and oxygen are, therefore, jointly responsible for red-shortness in commercial steels.

Alvin L. Davis,* Waterbury, Conn.—I have seen one case of the brittle effect of sulfur on pure nickel. Sheets that were perfectly malleable would become brittle when annealed, as sheet steel often is annealed, where gas similar to an illuminating gas is used. If the gas had much sulfur in it, it produced bars that were brittle on the outside; if exposed to the anneal long enough, they became brittle throughout and broke to pieces on subsequent cold working. Chemical analysis showed the presence of sulfur, and the microscope showed intergranular envelopes, which are characteristic of extreme brittleness.

Director of Research, Scovill Mfg. Co.

X-ray Evidence Versus the Amorphous-metal Hypothesis

By Robert J. Anderson,* Met. E., Boston, Mass., and John T. Norton,† Cambridge, Mass.

(New York Meeting, February, 1925)

The purpose of this paper is to report evidence, regarding metal structures, that is contradictory to the amorphous-metal hypothesis of Beilby, and particularly evidence that is opposed to the proposition that a vitreous amorphous layer is produced by polishing a piece of metal.

According to the theory of Beilby, which has been developed by Rosenhain and others, polishing a piece of metal greatly affects the condition of the metal at or near the surface polished, making that surface entirely different in character from the metal beneath. A vitreous amorphous surface film is said to be formed. The polishing process, on the basis of Beilby's explanation, is well known and does not require discussion here, but it is advisable to seek the precise meaning of the term "amorphous." According to Beilby, "amorphous means noncrystalline in the most intimate sense of the word; the molecules are not marshalled in crystalline order and orientation." According to Rosenhain, the amorphous condition is that assumed by a metal when the crystalline arrangement is completely broken up so that the atoms exist in a state of disorderly arrangement similar to that which exists in the liquid state. Thus, from the point of view of the phase rule, the "amorphous phase" is regarded as being identical with the liquid phase. Amorphous metal is often likened to an undercooled liquid. A crystalline substance is one in which the atoms are arranged in space according to some definite repeating geometrical pattern. The existence of amorphous metal has not been definitely proved.

The evidence offered here that amorphous metal probably does not exist is of a direct nature and is afforded by x-ray diffraction effects given by a number of metals and alloys when polished, cold-worked, and annealed. Considerable of the experimental work was carried out with substantially pure aluminum and the aluminum alloy duralumin, but many of the observations made on these materials were checked by similar observations on copper, iron, tin, zinc, lead, mild steels, and

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brass. The diffraction effects exhibited by these metals and alloys are doubtless exhibited by other metals and alloys; and while the discussion is based on data obtained in the *x*-ray examination of the materials listed, it will be evident that a general phenomenon is being dealt with.

At the outset, attention is directed to the results obtained in the case of diffraction patterns given by *x*-radiation impinging upon the surfaces of polished metals as related to the amorphous surface film of Beilby. The *x*-ray gives no evidence of an amorphous condition in the surface layer of a severely polished metal; perfect crystallographic diffraction patterns are obtained.

The experiments discussed here were carried out in the *x*-ray laboratory of the department of physics, Massachusetts Institute of Technology.

Apparatus, Methods, and Materials

As is well known, when a beam of *x*-radiation passes through, or impinges upon, a metal, or any other crystalline substance, the planes of atoms arranged in some orderly fashion, as a space lattice, act as a diffraction grating, thus giving particular diffraction effects; *e. g.*, lines or spots on a photographic film—lines when a modification of the powder method is used and spots or streaks when the Laue photographs are taken.

In the experiments discussed here, the diffraction effects were recorded with the standard General Electric Co. type of apparatus for *x*-ray crystal analysis, using monochromatic radiation.[1] A water-cooled Coolidge tube with molybdenum target operating at 22 to 24 milliamp. was used. The exposures were varied, depending on the material *x*-rayed, but 240 to 500 milliamp.-hr. covers the range employed. The metal samples were in the form of thin sheets, about 0.01 to 0.10 in. thick, thin wires, and metal powders.

In the powder method of *x*-ray crystal analysis (Hull-Davey) the substance for examination is finely ground, say to pass a 200-mesh screen or finer. Hull[2] mentions powder with grains 0.01 cm. in diameter, or less, as being suitable. When such a fine powder is placed in a small-bore glass tube, there is present a large number of crystals or grains arranged in greatly disordered orientation. Disordered or random orientation is essential, for to obtain a complete set of lines on the diffraction pattern it is necessary to have particles in the proper orientation to the incident beam of *x*-rays so as to give reflection from every possible family of atomic planes. Under certain conditions, rotation of the sample tube will increase the disorder of the orientation.

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[1] W. P. Davey: A New *X*-ray Diffraction Apparatus. *Genl. Elec. Rev.* (1922) **25**, 565.

[2] A. W. Hull: A New Method of *X*-ray Crystal Analysis. *Phys. Rev.* (1917) **10**, 661.

The powder method has serious disadvantages for the metallurgist, as in preparing a sample of metal powder the original physical condition of the metal is altered; moreover the method is not well adapted to the rapid routine examination of metals.

Two methods of obtaining the diffraction effects were used by the authors; these are referred to as the restricted-slit and the polished-surface. Both methods are modifications of the powder method, advantage being taken of the random orientation of the crystal grains of metals. In the restricted-slit method, the relatively broad band of *x*-radiation defined by the standard slit system of the diffraction apparatus is narrowed by a secondary slit arrangement, in order to give relatively narrow lines on the photographic film. This secondary slit arrangement also serves as a holder for the metal specimen. The sample for examination is preferably in the form of a thin sheet. The width of the slit may be about 0.005 in. for a sheet 0.01 in. thick; wider slits are required for thicker sheet samples. The width of the slit also depends on the metal to be *x*-rayed. The sheet sample, which may be, say, $\frac{3}{4}$ by $\frac{1}{2}$ in., is mounted on the secondary slit, which is placed on the cassette of the diffraction apparatus at the proper height, *i. e.*, the slit is held at the center of the circle about which the photographic film is bent. The secondary slit screens the sample of metal from the *x*-radiation except for a narrow band. The secondary slit is made of metal, which, of course, gives diffraction lines on the photographic film in addition to those caused by the metal sample, but the lines given by the former are fainter than those given by the sample, and if the holder is made sufficiently thick and of some metal having diffraction lines that are not easily confused with those of the metal being analyzed, no difficulty is had in interpreting the results. The authors have used restricted slit holders made of $\frac{1}{16}$-in. lead sheet.

In the polished-surface method, the beam of *x*-rays is diffracted by the planes of atoms situated in the surface of a polished piece of metal. A thin sheet or wedge of the metal is polished on a cross-section surface, and the sample is then so mounted that the radiation falls on the polished face. When the polished surface is suitably held in a horizontal plane, the beam of *x*-radiation strikes it at an angle of 5°, and the diffraction is caused in part by the surface atoms and in part by a portion of the radiation passing through the sample. Interesting effects are secured by tilting the surface at different angles. The polished-surface method has been used by various investigators (Davey, Bain, Lester).

The materials used in the experiments consisted of high-grade commercial metals and certain alloys, as follows: No. 1 aluminum (99.30 per cent. Al), electrolytic copper, electrolytic iron (99.97 per cent. Fe), electrolytic zinc, high-grade tin, soft lead, low-carbon steels, 66.67:33.33 brass, and duralumin (4 per cent. Cu, 0.8 per cent. Mg, 0.6 per cent. Mn, and remainder Al plus Fe and Si in subordinate amounts). The actual

chemical analyses of the materials are not pertinent to the present discussion.

Grain Size and Diffraction Effects

Cast or annealed metals have a relatively coarse-grain structure, while cold-worked metals have a fine-grain structure. With very severe cold work, the grain structure may be entirely obliterated, so far as microscopic examination can show. According to the Rosenhain conception of the mechanism of working, part of the crystalline metal is amorphized on work—amorphous metal being generated on the planes of slip. Bain, however, has shown that practically perfect crystallographic diffraction patterns are given by the most severely cold-worked metal obtainable. The authors have obtained typically good crystallographic diffraction patterns containing practically all the lines, in the case of aluminum reduced 97 per cent. by cold rolling and of electrolytic iron reduced 98 per cent. by cold drawing. That a cold-worked metal is totally crystalline, and not even partly amorphous, has, of course, been held by those who have rejected the hypothesis of amorphization on cold work (Heyn, Hatfield, Tammann, Guertler).

That the ordinary metallurgical microscope cannot reveal evidence of crystallinity, *i. e.*, grains and grain fragments, in a severely cold-worked metal is not proof of the absence of crystallinity. On Abbe's theory, von Rohr has fixed the smallest distance that an objective of aperture 1.40 can resolve at 0.00015 mm. From this, a grain or grain fragment at least 0.0002 mm. long should be distinguishable in a mass of cold-worked metal. The coarse grains of an annealed metal, on cold work, could easily be fragmented into smaller particles than this size and still be enormously large when referred to atomic dimensions. The grains of iron in martensite are submicroscopic, but martensite gives the crystallographic diffraction pattern of α-iron, as has been shown by Bain.[3] A grain fragment of aluminum (lattice parameter, 4.046 Å.U.) that is 0.00001 mm. long (0.00000039 + in.) would be about 3500 atom diameters in length, while one 0.0002 mm. long would be about 70,000 atom diameters in length (calculated from the distance of closest approach of the atoms as given by x-ray data). Obviously, grains and grain fragments of crystalline metal may be quite huge in respect to atomic dimensions, but still submicroscopic. In the powder method, if the substance is ground to pass 200-mesh or finer, the largest particle must be less than 0.074 mm. (0.0029 in.) long, assuming absence of needle-shaped particles. This is large compared to the size of grain fragments present in cold-worked metals, and a cold-worked, finely fragmented metal is certainly in suitable condition to yield crystallographic diffraction patterns.

[3] E. C. Bain: *X*-ray Data on Martensite Formed Spontaneously from Austenite. *Chem. & Met. Eng.* (1922) **26**, 543.

From theoretical considerations, it would be expected that size of grain should bear some relation to the appearance of the lines in the diffraction pattern, and Bain[4] has shown, for metals, that this is the case. A fine-grained metal gives straight sharp lines on the diffraction pattern, while a coarse-grained metal gives dash lines. In the powder method, if the particles are too coarse, the pattern shows dashed lines. With very coarse-grained metal, only several dashes may be obtained on the film; but with fine-grained (cold-worked) metals narrow sharp bands are given. As the grain fragments increase in number and decrease in size, the straight narrow bands tend to become wider. The authors have found, with large single crystals of aluminum, that only one or two dashes appear on the film.

From the law governing x-ray reflection, it is evident that a family of planes in a particle must make a definite angle with the incident beam in order to give an image on the film. But as the sample is of finite size, there is some latitude that the position of the particle may have and still make the proper angle for reflection. Each crystal grain forms an image of the projection of the target on the film, and these images will completely overlap and give a smooth straight line if the crystal grains are small enough. If the grains are not small and numerous, these images, which are lenticular-shaped spots, may not completely overlap, consequently the dashed or striated lines are obtained. The chances for reflection increase with increase in the number of grains. A single crystal has the least chance of being suitably oriented to reflect; the chances are increased greatly with coarse-grained metals, and dash lines are given; the chances are so many with cold-worked metals that the reflections overlap and solid lines result.

Effects of Cold Work and Anneal on Diffraction Lines

A large number of spectrograms were taken in the course of the experimental work and show the effect of mechanical and thermal treatment on the x-ray diffraction lines given by metals. The authors have checked a number of Bain's observations and have obtained some new data. Sharp solid lines in the diffraction patterns have been observed for aluminum, when broken cold by rolling in the range 10 to 97 per cent. reduction in area; cold-rolled duralumin, brass, and steel; cold-drawn iron wire; and cold-forged zinc, and lead. When annealed, all of these materials give dashed lines. Only a few typical patterns are shown to illustrate the effects obtained: Fig. 1 shows the sharp solid lines in the pattern of cold-rolled aluminum sheet and Fig. 2 shows the dashed lines given by the same metal when annealed for 1 hr. at 500° C. and cooled in

[4] E. C. Bain: Studies of Crystal Structure with X-rays. *Chem. & Met. Eng.* (1921) **25**, 657; and *op. cit.*

the furnace. Fig. 3 shows the dashed lines (above) of duralumin sheet, air-quenched from 500° C., and the solid lines (below) of the same material as cold rolled.

Some samples were stressed under various loads in a tensile machine and then *x*-rayed, while other samples were put under tension in a suitable holder and *x*-rayed while under stress. It was found that tensile loading tends to make the normal dashed lines of annealed metals solid, greater loads, up to a certain amount, giving greater sharpness of the lines. The conclusion to be drawn is that greater deformation by tensile stressing causes increasing fragmentation of the original grains of the annealed metal, as would be expected; the proof is in the appearance of the diffraction lines. Thus, taking well-annealed aluminum; a small load (2000 lb. per sq. in.) sharpens the lines and causes them to straighten out somewhat, as shown in Fig. 4, while a large load (10,000 lb.) causes the lines to straighten out completely and become as sharp as in the case of metal heavily cold-worked by rolling, as shown in Fig. 5. Fig. 6 shows the dashed lines given by annealed mild steel and by the same steel under a load of about 25,000 pounds.

Diffraction Patterns Produced by Polished Surfaces of Metals

One of the most important observations arising from the experiments resulted from systematic study of the effects produced by the diffraction of *x*-radiation by polished surfaces of metals. On the basis of the generally accepted definition of amorphous metal, it should be expected that *x*-radiation diffraction by a polished surface of metal would not give the crystallographic diffraction pattern typical of a particular metal, but rather that it would give general blackening or simply broad bands as do certain liquids. The authors are aware that *x*-ray data have indicated an amorphous condition in metals, but the data so far presented are neither numerous nor convincing. As stated by Wyckoff,[5] diffraction effects different from those given by crystalline matter ere given by crystals in which the normal regularity of atomic arrangement is, for some reason, incomplete or imperfectly maintained; and by matter that is not in the crystalline state. In Laue photographs of diffraction effects of strained crystals, the normal (for a perfect single crystal) Laue spots are elongated into radial streaks; it has been suggested that these streaks are essentially powder photographs produced by minute crystals in positions that deviate somewhat from the parallelism of the main body of the crystal.

[5] R. W. G. Wyckoff: "The Structure of Crystals," 371–391. The Chemical Catalog Co., New York, 1924.

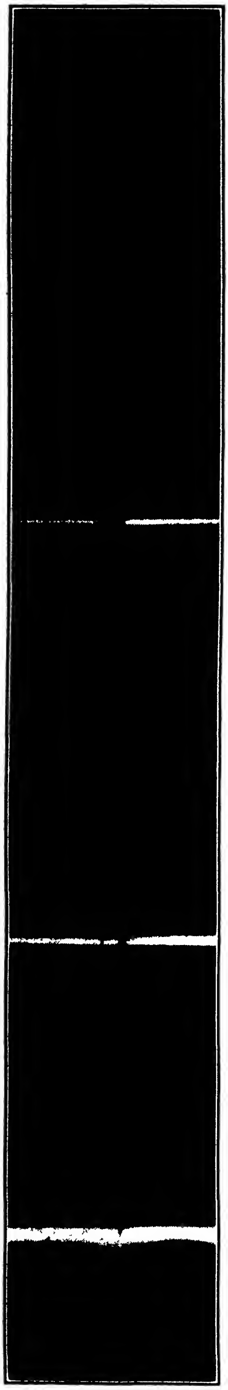


FIG. 1.—DIFFRACTION PATTERN OF SEVERELY COLD-WORKED ALUMINUM SHEET—SHARP SOLID LINES.

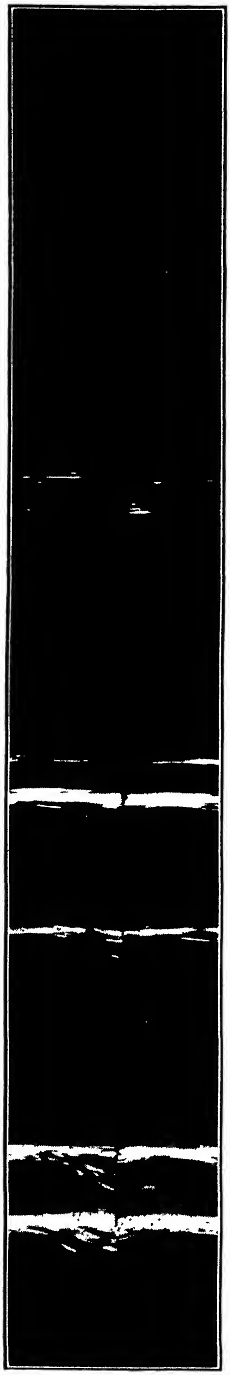


FIG. 2.—DIFFRACTION PATTERN OF WELL-ANNEALED ALUMINUM SHEET—WAVY DASHED LINES.

FIG. 3.—DIFFRACTION LINES OF DURALUMIN SHEET; TOP, AIR-QUENCHED, DASHED LINES; BOTTOM, COLD-ROLLED, SOLID LINES.

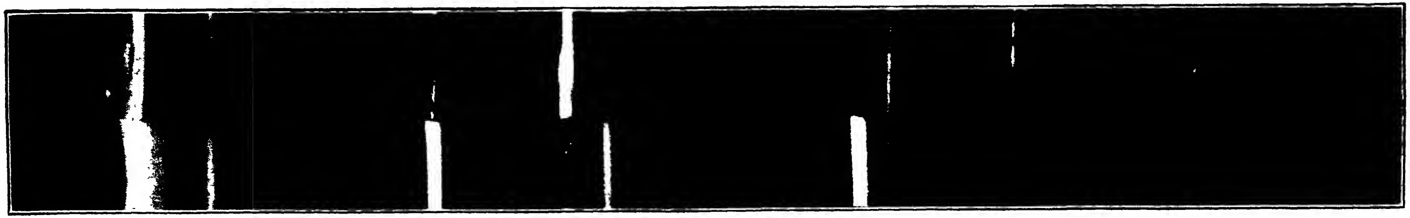


Fig. 4.—Diffraction lines of aluminum sheet; top, dashed lines of annealed sheet partly straightened by stress of 2000 lb.; bottom, solid lines of hard-worked sheet.

Fig. 5.—Diffraction lines of aluminum sheet: top, solid lines of hard-worked sheet; bottom, dashed lines of annealed sheet made solid by stress of 10,000 lb.

Fig. 6.—Diffraction lines of steel; top, dashed lines of annealed steel made solid by stress of 25,000 + lb.; bottom, normal dashed lines of annealed steel.

Referring to the blackening of the film or general scattering of the radiation from a crystalline substance, Debye[6] has pointed out that increased amplitudes of atomic vibration do not alter the relative positions of x-ray diffraction effects, but do decrease their intensities. Hull[7] has found only a general blackening on the powder photograph of metallic potassium, while sodium gave quite faint lines on a blackened field. The interpretation of this effect would be that potassium is amorphous. However, potassium has the sharp melting point typical of pure metals in general, and it gives a typical crystallographic diffraction pattern at −150° C. As Wyckoff points out, it is quite probable that at room temperature the amplitudes of the thermal vibrations of potassium atoms are great enough to obliterate the crystalline diffraction maxima. In passing, it should be stated that the diffraction of radiation by most liquids gives not a general (amorphous) scattering but a series of one or more broad diffraction bands. Liquid mercury gives no pattern, as would be expected.

It is plain that if a polished surface of metal should diffract the x-radiation so as to give the typical pattern of the crystalline metal, the only conclusion that can be arrived at is that the polished layer is not amorphous (*i. e.*, disordered as to atom arrangement), but truly crystalline. The authors have shown that typical perfect crystallographic diffraction patterns are given by heavily polished metal surfaces, thus showing that the presumed amorphous surface layer is simply made up of crystalline fragments. The diffraction lines given by a burnished surface of metal are quite similar to those given by a heavily cold-worked metal. A heavily cold-worked metal, or the severely polished surface of a piece of metal, may be so finely fragmented that the crystalline character is not visible microscopically, but its truly crystalline nature is shown by the x-ray diffraction pattern. While the fact that there is no amorphous metal present in a cold-worked metal or in the polished surface layer of a piece of metal cannot be proved by the evidence submitted here, such materials cannot be amorphous, nor anything like amorphous, and give crystallographic diffraction lines.

A well-annealed sample of metal gives a dashed-line diffraction pattern when examined by the restricted-slit method. When a surface of such a sample is heavily burnished, and this surface is used to diffract the radiation, the resulting pattern shows sharp solid lines corresponding to the planar spacings. When, however, the polished surface of such an annealed sample is etched sufficiently to remove the worked surface

[6] P. Debye: Über die Intensitätsverteilung in den mit Röntgenstrahlen erzeugten Interferenzbilden, *Ber. Deutsch. Physik. Gesell.* (1913) **15**, 738; and Interferenz von Röntgenstrahlen und Wärmebewegung. *Ann. der Phys.* (1914) **43**, 4th ser., 49.

[7] *Op. cit.*

layer, and this etched surface is used to diffract the radiation, the resulting pattern shows the dashed lines characteristic of the annealed metal, as would be expected. The thickness of the polished surface layer is variable, depending on the amount of the polishing and the kind of metal dealt with, but the thickness varies from say 500 to 5000 $\mu\mu$; in the case of aluminum, this is a layer 1800 to 8800 atom diameters thick.

Fig. 7 shows the straight lines given by the surface of annealed aluminum that had been heavily polished. There is a slight indication of dashed lines, doubtless due to diffraction by larger grains of metals below the polished surface, if the penetration was sufficient, or from the radiation passing through the sample and being refracted up through the polished surface layer or through the lead backing. The faint lines are those given by the lead backing. A lightly polished piece of well-annealed metal, or a piece polished and then etched, never gives solid lines, but always dashed. Fig. 8 shows the solid lines (below) of a burnished surface of annealed aluminum and the dash lines (above) of the same surface after etching. This film was taken on a single piece of metal split on the septum, half of the burnished surface having been etched. Interesting effects are obtained when burnished surfaces of annealed samples are tilted so as to throw lines farther from the zero end of the film, *i. e.*, to strengthen the remote lines which are often weak. The sample may be tilted or the surface ground at an angle with the horizontal. A spectrogram of such a sample shows solid lines most remote from the zero end, while those near the zero end are broad and confused, showing effects secured from a combination of relatively widely separated dashes (given by the large grains of the annealed mass) and straight lines (given by the worked surface layer). Fig. 9 shows a pattern given by annealed aluminum with a burnished surface, tilted forward 30° from the horizontal in the direction of the x-ray tube.

Most striking are the results obtained by x-ray diffraction from polished surfaces of large single crystals. A single crystal gives ordinarily one or two dashes on the film and sometimes a short doublet line. The polished surface of a single crystal gives the lines of the crystallographic diffraction pattern. The pattern may not be perfect, but this is the result of insufficient thickness of the burnished layer, *i. e.*, an insufficient number of fragments suitably oriented. When the polished surface of a single crystal is deeply etched to remove the worked layer, the diffraction of the radiation by such an etched surface gives no pattern at all; or more precisely, it gives one or two dashes and at times a blur on the film, just as when the radiation is "shot through." Fig. 10 shows an imperfect line pattern given by a polished surface of a large single aluminum crystal (the crystal was about 1¼ by ½ in.). The same crystal gave only one or two dashes and a short doublet line on "shooting through" or diffracting with an unpolished surface. Fig. 11 shows the spectrogram

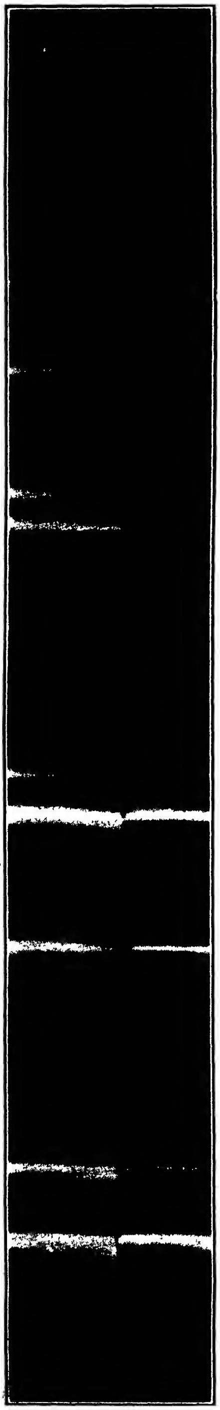


FIG. 7.—SOLID-LINE DIFFRACTION PATTERN OF BURNISHED ALUMINUM (ANNEALED) SHEET SURFACE.

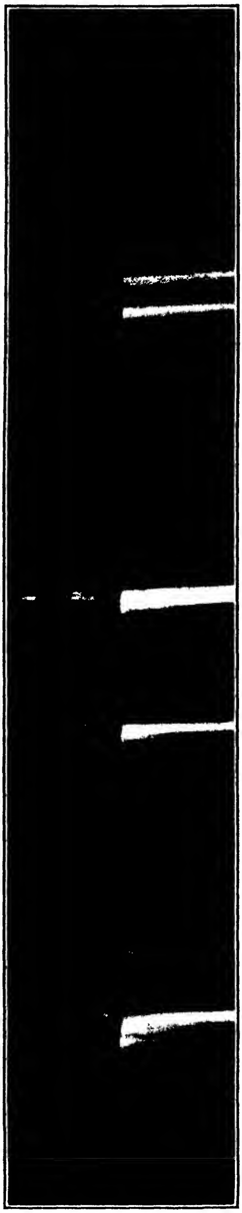


FIG. 8.—DIFFRACTION PATTERN OF ANNEALED ALUMINUM SHEET: TOP, DASHED LINES FROM BURNISHED SURFACE AFTER ETCHING WITH HF; BOTTOM, SOLID LINES FROM BURNISHED SURFACE.

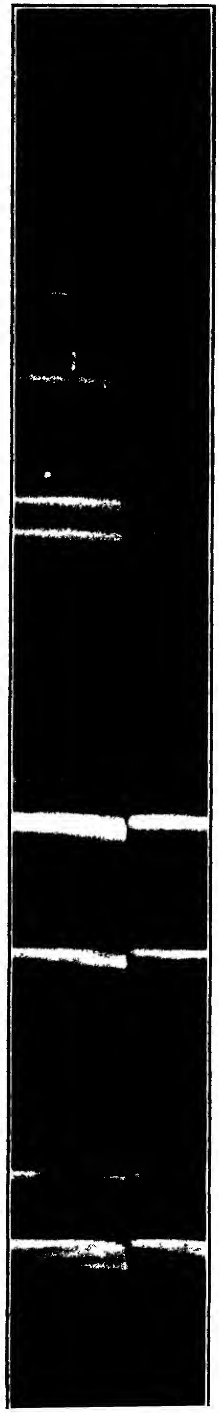


FIG. 9.—DIFFRACTION PATTERN OF BURNISHED ALUMINUM (ANNEALED) SHEET, TILTED FORWARD.

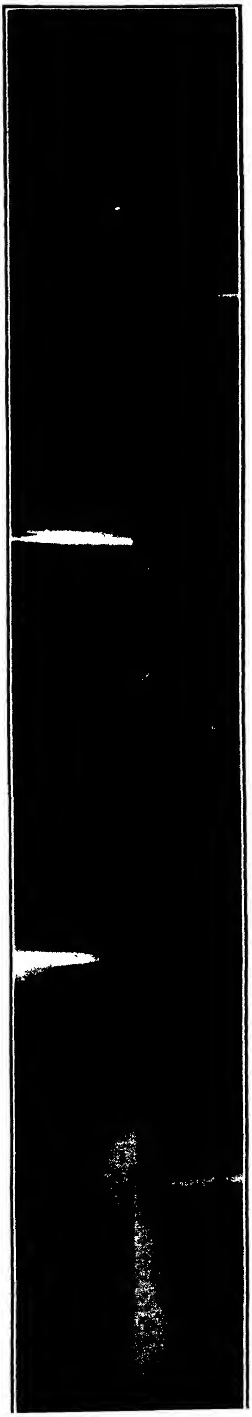
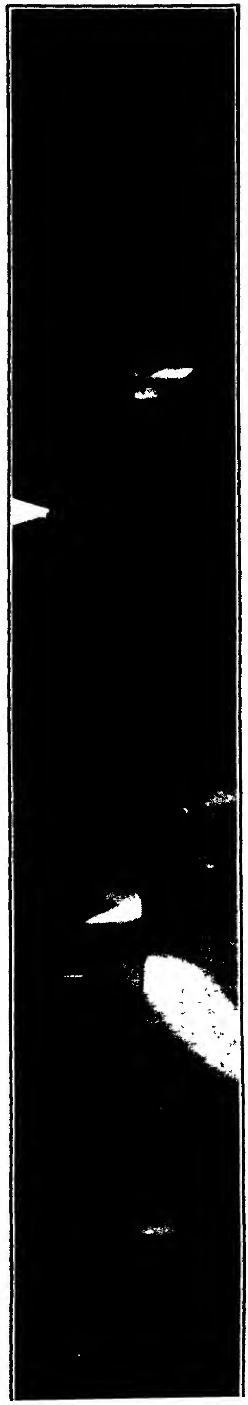


Fig. 10.—Solid-line diffraction pattern given by a surface polished on a large single aluminum crystal.



11.—Diffraction effect given by a surface polished on a large single aluminum crystal, subsequently deeply etched with HF.

given by a polished and etched surface of a large single aluminum crystal. The effect is quite similar to that given by unpolished single crystal surfaces, although there are more diffraction markings than is usual. This may be due to insufficient etching, part of the polished surface not being removed. In Fig. 10, the strengthening effect of metal underlying the polished surface layer is not had, as is the case with Fig. 7, but the pattern is quite definite. It is, of course, understood that photographs made from *x*-ray diffraction films of the type dealt with here lose much in reproduction and are not nearly so good as the films.

Résumé and Conclusions

The effects of cold work, polishing, and anneal on the appearance of the *x*-ray diffraction lines given by a number of metals and alloys have been discussed, and the evidence obtained indicates that metals are not amorphized by cold work or polishing. The paper may be summarized briefly as follows:

1. Two methods for taking *x*-ray diffraction patterns of metals have been described and their advantages over the powder method pointed out.

2. Severely cold-worked metals, reduced as much as 98 per cent. in area, give true crystallographic diffraction patterns.

3. The appearance of the lines in the Hull diffraction pattern is affected by the grain size of the metal.

4. Cold-worked (finely fragmented) metals give sharp solid lines in the pattern, owing to the overlapping of reflections by a great multiplicity of atomic planes oriented at suitable angle to the beam of *x*-radiation.

5. Annealed (coarse-grained) metals give dashed lines in the pattern, owing to separate reflections from few atomic planes suitably oriented to the radiation.

6. The polished surface of a piece of metal when used to diffract *x*-rays gives sharp solid lines in the pattern, this indicating a fine-grained structure.

7. The fact that polished surfaces of metals give crystallographic diffraction patterns shows that there is not a vitreous amorphous film in the surface but simply a great multiplicity of crystal fragments.

DISCUSSION

Zay Jeffries, Cleveland, Ohio.—The *x*-ray spectrometer is an instrument that will show positively the presence of crystalline material under certain conditions; it will not show positively the absence of amorphous material, especially when there is supposed to be a mixture between vitreous amorphous on the one hand and crystalline material on the other. So much has been said on the general subject as to the Beilby theory by myself and my associates, that our position is pretty well defined. We

pointed out that Beilby's theory of the development of a vitreous amorphous substance hard enough to prevent further slip was untenable. During the deformation of a metal like copper, where these slip planes are used over and over again, there is no other way to account for the deformation except by the use of many of the slip planes over and over again.

The conclusion is drawn, then, that there is no hard vitreous amorphous metal at the planes of slip during mechanical work which is materially stronger than the potential slip planes; in fact, in many cases, those planes on which slip has already occurred are very much weaker, as in the case of pure iron freshly deformed.

In the case of polishing, there is a much better chance to change the metal into an amorphous condition, or a condition that is substantially amorphous, than in cold work. You then have the action of an abrasive on the surface of the metal traveling over tremendous distance. When you consider the speed of the polisher's wheel and the number of rotations and the time the piece is held against the polishing wheel, the outer layer might be vitreous amorphous and be totally missed in any examination of this sort. So that the paper does not disprove the existence of any amorphous metal.

Chu Phay Yap, Golden, Colo. (written discussion).—While the writer cannot agree with Rosenhain's assumption that an amorphous phase exists in a large quantity as a result of either cold-working or severe quenching, *e. g.*, as in martensite, he thinks that it is most likely that the so-called amorphous phase actually exists to a limited extent in the polished surface of a specimen, and in the grain-boundary regions among crystals adjacent to one another.

It seems very likely for the atoms in the grain-boundary regions to be unordered with respect to any particular lattice spacing as the result of the different orientations of the attracting and repulsing atomic forces. The atoms thus unoriented (*i. e.*, amorphous) may be conceived to be held in some stable equilibrium by the resultant of all the atomic forces acting upon them, and thus, unless any particular crystal is capable of entirely overcoming this resultant force, it cannot induce these unordered atoms to arrange themselves according to its lattice spacing.

If severely cold-worked metals still show a distinct spectrogram, it does not necessarily follow *a posteriori* that an amorphous phase does not exist. We shall be equally justified in concluding that the numerous, highly fragmented and submicroscopic crystals are still able to diffract the rays even in the presence of any amorphous material, by using the following analogy: If the Hull-Davey powder method gives us a pattern despite the fact that there must be a large percentage of air voids between the different powdered crystals, then it would be equally reasonable to expect a pattern from a severely cold-worked specimen even if a large

percentage of the material were in an amorphous state. If we could definitely prove by actual demonstration that the amorphous phase, as it exists in cold-worked metals, does not show a spectrogram, the only remaining conclusion we could draw from the findings of the authors would be the well-known fact that very minute crystals are always able to give a diffraction pattern. Ordinarily, the burden lies on the supporters of the amorphous theory to prove that the so-called vitreous phase in the grain-boundary region is or is not able to give a diffraction pattern, but in order to argue against the existence of an amorphous phase even in a highly cold-worked specimen, the authors must prove theoretically or empirically that an amorphous phase, were it present, is incapable of diffracting the x-rays. The atoms in the amorphous phase, by definition, are not arranged in any regular lattice spacing, and yet it is possible to have a layer of atoms in this condition (that is, the atoms may be intersected by a plane) and it is also possible to have several parallel layers. In such an event, it might not be too absurd to imagine the possibility of a diffraction pattern, when the substance is subjected to a beam of x-rays.

We have already derived indirect, but rather convincing, proofs of the existence of an amorphous phase in a highly cold-worked metal or in the polished surface of a specimen. The phenomena of an intercrystalline fracture at high temperatures versus an intracrystalline fracture at low temperatures, the experimental evidence that a fine-grained specimen shows a higher vapor pressure than a coarse-grained specimen, and the fact that the mass hardness (by the scratch method) of a polished surface is higher and more uniform than any unpolished part of the specimen, are all indirect proofs of the existence of an amorphous phase. Of course, the higher hardness of a polished surface may be also due to the extremely severe fragmentation of the crystals on the surface, but again, we have as yet no adequate reasons to account for this increased hardness unless we take advantage of the amorphous hypothesis. Also, it seems rather difficult to account for the uniform hardness of a polished surface without the aid of the amorphous hypothesis.

The conclusion that "the fact that polished surfaces of metals give crystallographic diffraction patterns shows that there is not a vitreous amorphous film in the surface but simply a great multiplicity of crystal fragments," does not necessarily follow from the experimental evidences obtained, for the following reasons:

1. The x-rays, according to Bragg, are able to penetrate as deeply as 1 mm., although that is not generally the case. The thickness of the polished specimens used by the authors, according to their own statement, varies from 500 to 5000 $\mu\mu$, and even if the film were amorphous, a pattern might be obtained due to the diffraction by the crystalline matter underneath the film.

2. The polishing operation is such that we would expect crystal slip in a direction parallel to the surface of the specimen. It is then possible that within the amorphous film itself may be different layers of atoms all parallel to the surface. These atoms do not belong to any particular crystal, but to different crystals, and the deformation of their original lattice is such that the atoms may be spoken of as "leveled" and capable of being intersected by a plane. The film itself may then be able to give a pattern if there are enough layers of these atoms to diffract the rays.

3. The process of polishing may be such that although the film appears to be entirely amorphous, there is a possibility of very minute and submicroscopic crystals highly dispersed in the film. In such an event, it also seems reasonable to have a diffraction pattern if the rays were stopped and diffracted within the thin amorphous film.

The experimental evidence adduced by the authors, therefore, does not *per se* prove the absence of the amorphous phase. There is some amorphous material within the grain-boundary regions, as a result of either quenching or severe cold-working. Most likely the film is not entirely amorphous, but the amorphitization is sufficiently marked to obliterate all microscopic evidences of crystallinity.

Francis B. Foley,* Chattanooga, Tenn. (written discussion).—There is no doubt in the minds of those who have occasion to polish metals for microscopic examination that the surface of the metal is often changed in the process of polishing. It is often necessary, particularly when preparing surfaces on soft metals, to etch and repolish lightly a number of times before a surface giving the true structure of the metal is obtained. Many poor and misleading photomicrographs are no doubt the result of etching this superficial surface layer of altered metal. A determination that this layer is not amorphous is purely academic, but in the broad question of whether or not metals do generally have an amorphous phase is important in clarifying one general conception of how they act under various conditions of working and of temperature. The authors have apparently driven another spike in the coffin of the general amorphous-metal hypothesis which has been reared a weakling from its inception.

One of the arguments commonly advanced in favor of the amorphous-metal hypothesis uses it to explain the fact that metals fail by intercrystalline fracture at high temperature and transcrystalline fracture at low temperature. It is said that an amorphous layer cements crystals together and that the amorphous cement is plastic and yields when hot but is rigid as glass at low temperatures. There is something else that will explain this difference just as satisfactorily as the amorphous cement theory does, but no one seems to have used it yet.

* Metallurgist, Lucey Mfg. Corpn.

Crystals grow in metals at high temperature. This growth of crystals probably takes place by the robbing, atom by atom, of one crystal by its neighbor. Growth would seem possible also by the process of one crystal annexing another whole crystal as a unit. Those who have studied the matter will indorse the atom by atom system of growth. In the atom by atom process, there must be greater activity of the atoms at crystal boundaries in metals at high temperature than in the center of the crystals because there is readjustment of atoms robbed from one crystal

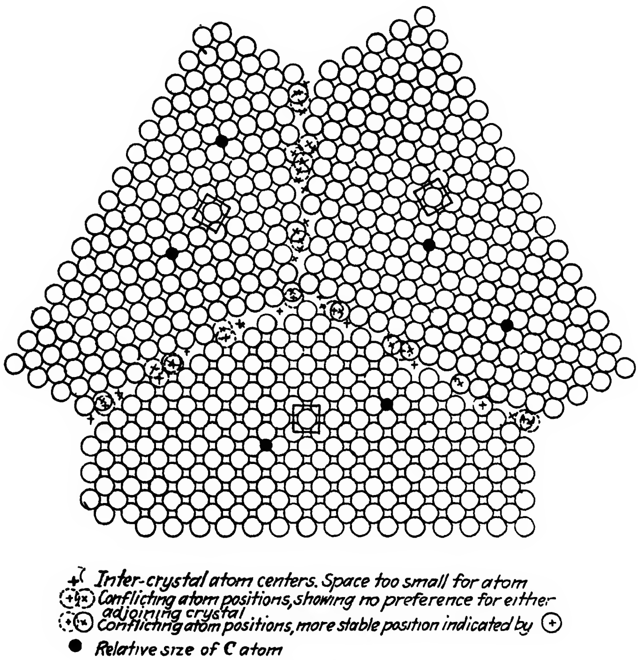


FIG. 12.

by another. The crystal boundaries are moving and the atoms that go to make up the crystal boundaries are moving and changing. When a stress is applied to hot metal the parting naturally comes in this transitory region and one could easily imagine some atoms being caught at the moment when they had just gotten out of control of one crystal and had not passed into the complete control of their new host. Such atoms might be lost as impalpable atomic debris or might readily go into chemical combination with the oxygen of the air.

At low temperatures, where there is little if any grain growth, the irregular crystal boundaries offer greater resistance to slip than the even planes of atoms within the crystals, and failure takes place through the body of the individual crystals.

Fig. 12 is a conventional drawing in a plane of the meeting of three crystals. The circles are atoms of iron and the lattice is face-centered cubic. The drawing was made by starting at three random points and building up three crystals by the addition of atoms until the three crystals met. The "X's" represent optional atom centers—that is where two or more centers which belong in the adjoining crystals conflict, with room for a smaller number of atoms. There is often a more stable position in one crystal than in the other and the atom center of the more stable position is used and the atom drawn in solid, the optional position in the adjoining crystal being dotted. At times there is an atom center but no room for an atom—in which event there is no atom and none is drawn. Such a diagram does not show much room for an intercrystalline amorphous cement. There are, of course, some atoms that might as readily join one crystal as its neighbor, and one wonders if it is not such atoms that are the underlying cause of grain growth, for it may be that under conditions of atomic vibration the jumping of an atom from its position of doubt to one of the adjacent crystals might cause a stampede of atoms to the one chosen, or perhaps from it. It appears, from this diagram, that a space exists at various points along the grain boundaries. The atoms along the grain boundary would probably space themselves to take up much of this space and for some atom rows deep on each side of the grain boundary there might be a slightly wider spacing which would disappear gradually. This refers to the cold state when the atoms are relatively at rest and would result in a slight distortion of the space lattice in the neighborhood of grain boundaries. Such a condition would give rise to greater strength locally. As has already been stated, grain boundaries are not permanently fixed at elevated temperatures. The circles in the figure representing iron atoms, the magnification would be 10,000,000 diameters.

H. H. Lester,* Watertown, Mass. (written discussion).—There is a very definite question as to amorphous layers as Rosenhain defines them, particularly at grain boundaries. It seems to the writer, however, that the experiments described do not go quite far enough to settle definitely the question as to the existence of these layers. No doubt not much, if any, amorphous layer exists at a polished surface, but if such a layer does exist it probably does not extend many atoms deep and ought to be underlaid by a region of broken-up crystals. X-ray penetration, particularly in the case of aluminum, would be sufficient to give a spectrum from the broken crystals beneath the amorphous surface layer. Such spectra would exhibit the phenomena described by the authors, but would hardly prove that the amorphous layer does not exist. The effect of the amorphous layer, if it is present, would be seen in a general darkening of the

* Research Physicist, Watertown Arsenal.

whole photographic film, the extent of the darkening depending on the relative amount of amorphous constituent present.

We have found, at Watertown, that troostitic and sorbitic steels do not give as clear photographic films as the same steel carefully normalized. In fact, the clearing up of the film seems to be coincident with the development of the carbide spectrum. We have considered the general darkening to be due to the presence of carbon in atomic dispersion or else to carbide particles so small that they have the general darkening effect to be expected from amorphous material.

It is possible that the general darkening of the photographic film due to an amorphous layer on a polished surface would be too small to measure. It seems to the writer, however, that a comparison of the general blackening of the photographic film from etched and unetched specimens might give information of somewhat greater value than that reported in the present investigation.

EDGAR C. BAIN,* Long Island City, N. Y. (written discussion).—I have been greatly pleased to find that my own early work with the x-rays has been repeated by the authors with results substantially in agreement with my own. Those of us who have pioneered in the field of the application of x-rays to metallurgy, perhaps more than any other group, feel the need of independent checks on our experimentation, because the method is involved, difficult, and unique.

The authors are to be congratulated on the excellent results they have obtained with the x-ray equipment. Because of the excellence of their apparatus, their discoveries are the more significant. The proof of the existence of a material or a phenomenon is comparatively easy. Complete proof, however, of the absence, in toto, of a material or a phase is a much more difficult proceeding. Without any intent to disparage the highly significant conclusions of the authors concerning the atomistics of cold work and deformation, I should like to present a consideration of the data leading to the suggestion of the non-existence of the amorphous film. It seems highly likely that the process of grain fragmentation is the most important one that takes place during cold working, but I believe that we are scarcely able to say, even from the data presented in this paper, that we have conclusive proof, or even significant evidence to disprove the existence of the amorphous film of Beilby. To test this hypothesis, I obtained the x-ray spectrogram of a thin sheet of aluminum by the surface-reflection method with a specimen of copper lying below the aluminum. The thickness of the aluminum sheet was 0.0008 in., a far greater thickness than we should expect of amorphotized material; nevertheless, the dominant pattern recorded on the film was not that of aluminum, but of the copper beneath. Hence, the writer believes that

* Research Metallurgist, Union Carbide & Carbon Research Laboratories, Inc.

in all films of aluminum and aluminum alloys the x-ray crystallogram is built up from the diffraction of materials lying at much too great a depth below the surface of the specimens to give evidence of the nature of that surface.

In this experiment, a very coarse-grained copper was used, so as to give a characteristic pattern of the sub-layer. The fact then, that this easily distinguishable pattern of copper contains by far the greater portion of the energy can leave no doubt that it is the deep layers, even in the reflection method, that are responsible for the diffraction pattern. The

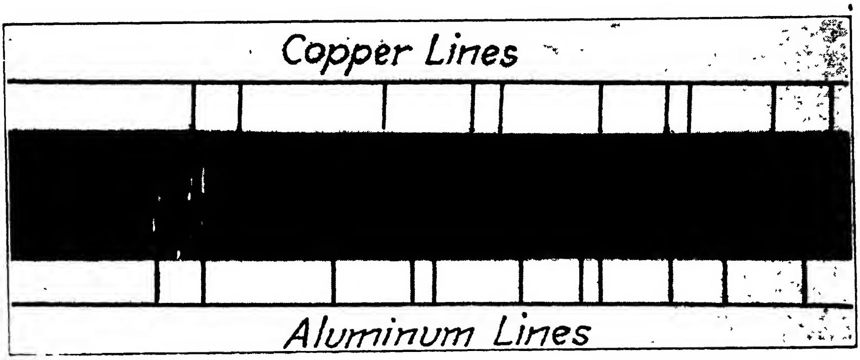


FIG. 13.

authors have admitted this general circumstance to be true, but they attach undue significance to the fact that, instead of obtaining no pattern at all from their samples, they did obtain a strong aluminum spectrogram. The point is that even had there been an amorphitized layer of perhaps 0.001 in., the pattern would have been that of ordinary crystalline aluminum, and we are in complete agreement, I believe, that if there be any amorphous layer on the surface of the burnished metals, it has a thickness very much less than 0.001 in. Fig. 13 illustrates the strength of the spectrogram obtained from the underlying copper.

ANCEL ST. JOHN,* New York, N. Y. (written discussion).—It is pertinent, however, to present here a lantern slide that was exhibited at a meeting of the American Physical Society in Boston in December, 1922. This illustrates my method for obtaining very sharply defined and accurate crystal patterns by means of a slit in contact with the specimen on the side toward the photographic film. As neither of the authors was present at this meeting, and as the only published description of the method is an incidental reference in the course of a short note on the structure of manganese dioxide printed in the *Physical Review* for March,

* Consulting Physicist.

1923 (p. 389), the authors are to be pardoned for overlooking this previous publication of what they call the restricted-slit method.

L. W. McKeehan,* New York, N. Y.—One thing is evident on Figs. 4 and 5 that is not mentioned by the authors but which may be of interest in connection with some other recent work; *viz.*, the great difference in the distribution of intensities between the lines of the two photographs shown in each of the figures. The upper pattern in Fig. 4 and the lower pattern in Fig. 5 are more nearly what we expect in a random arrangement of crystals. The pattern in each case, however, shows marked enhancement of the line that may be identified as caused by reflection from the (311) planes of the crystal (the fifth strong line from the left-hand side of the diagram) and this is probably caused by the process of stretching, which has turned some of the (111) planes nearly at right angles to the plane of the sheet. The (311) planes are then inclined at such an angle to the x-rays in this arrangement, which Doctor St. John's slide shows, that they are particularly well placed for reflection. There are other differences between the patterns, pointing to the same conclusion. One is the weakness of the first and second order reflections from the (100) planes in the stretched material.

Carle R. Hayward,† Cambridge, Mass.—How much crystalline material must there be on a surface to give an x-ray photograph like the one shown? As an analogous illustration, if one takes some putty and spreads a few grains of sand in it with a putty knife, how many grains of sand would be necessary to produce the crystalline characteristics? In view of what Mr. Bain has said, perhaps that is not pertinent for, if the x-ray penetrates through the film, I can hardly see how we are to prove whether amorphous material is absent or not.

Ancel St. John, New York, N. Y.—I have exposed 0.02 gm. of powdered copper distributed in an inert powder that gives no x-ray pattern in a container approximately ¾ in. square and ⅛ in. thick and have obtained a distinct pattern. Figuring out the effect of the copper on the basis of 0.02 gm. to 3.00 sq. cm. of surface will give some idea of how little copper can produce an x-ray pattern. That would correspond to an exceedingly thin film upon the surface; and if distributed over the surface, the conditions are much more favorable for reflection than they are in the method I used.

R. P. Heuer, Philadelphia, Pa.—This x-ray method seems to be qualitative as a test for crystalline material but it is not quantitative. Perhaps we might introduce here the more quantitative processes of thermodynamics. If we consider entropy as a measure of the random-

* Western Electric Co.

† Associate Professor of Metallurgy, Massachusetts Institute of Technology.

ness of any system, the single crystal and an "amorphous metal" layer would exhibit different entropy. Having different entropy "amorphous metal" would exhibit an electrode potential differing from that of the single crystal. Data on the potentials of these single crystals and their polished surfaces might furnish interesting evidence.

Jerome Alexander,* New York, N. Y.—I want to come out flat-footedly against the amorphous point of view. What is called amorphous metal mainly consists of exceedingly fine crystals of some form. Some work is now being done on metals of this character by Professor Sherrer, at Zurich, and such evidence as he has brought out seems to indicate that there is no reason whatsoever why we should not have atoms and minute crystals coexisting in the same dispersion. I think it is extremely likely that in every case there would be some few isolated atoms or molecules. We cannot call a phase an amorphous phase because there are a few atoms that have not found their place in a crystal lattice. We must be governed by the condition of the preponderance of the particles existing.

A great deal of confusion is introduced into these questions by the mental concept "amorphous," because we are pushing further and further down our means of observation. Formerly we used to look at things with the microscope. Then Zsigmondy developed the ultra-microscope which brought into view many things existing below the level of microscopic visibility. With the x-ray spectrometer we have discovered that molecules are not homogeneous. We must get away from the idea that "amorphous" is in every way coincident with "homogeneous," because it is not; the two terms are not synonymous, although popularly they are believed to be.

Beilby and Rosenhain say that in amorphous metal, the molecules are in the haphazard or totally random distribution that exists in liquids. From what little I know of the properties of metals, I cannot conceive that that is true, and may mention some evidence acquired from sulfur. I used sulfur because I could work with it readily, which I could not do with metals. I dissolved some sulfur in carbon disulfide with a little Canada balsam as a retarder, and put a drop of the solution on a slide, rubbed it out, and blew on it so that the solvent evaporated rapidly. In the ultra-microscope, the slide showed many interesting things. In the first place, there were a large number of small spherulites, many of them ultra-microscopic in size; also aggregations of these spherulites. A large number of the spheres grouped themselves together in a chainlike effect; another aggregation was cluster-like. In addition, bordering these structures, were definitely formed crystals. Immediately surrounding the crystals were vacant areas, which indicated that each

* Consulting Chemist.

crystal had reached out and dragged to itself, as far as its molecular arms would reach, all the spherulites in that neighborhood. At many places these ultra-microns or spherulites were sticking to the crystals, showing that they tried to work their way in but could not find lodgment in the crystal lattice. This indicates that in sulfur, in any event, the building up of crystals does not necessarily proceed molecule by molecule, but that preliminary groups form and these preliminary groups then form aggregates.

I think investigation will prove that the same thing exists in metals, because we all know the aggregation tendency of metals is exceedingly powerful. In 1905, Benedicks brought out the view that colloidal dispersion was to be considered in connection with metals. In 1920, Donnan unearthed, at the University College, London, a doctor's thesis presented in 1896 by H. Kneebone Tompkins, but never published, that discussed the analogies with colloids of a great many substances, particularly rubber and metals.

In the colloidal state, if the viscosity is not too great, the action of the particles becomes greatly intensified if the dispersion becomes a little bit finer, so there may be migration of particles or molecules in masses, instead of individual molecules moving one by one.

Carl Benedicks,* Stockholm, Sweden.—In the case of the amorphous theory, according to our view, it is necessary to question what is the use of this assumption, and then we must say that the essential thing was to get an explanation of the hardness of metals by cold working. It is not necessary to have recourse to that view.

We should not reject an idea absolutely because we have no proof of its necessity. Now, if in metals it is possible to approach to an amorphous state, it will be by having an alloy of a low melting point squeezed out at low temperature so as to form a wire. It is easy to bend this wire in any form just as you like if you proceed very slowly, but on proceeding quickly, it is immediately broken. That is the most characteristic property of amorphous substances and one has the right to say that such a squeezed-out metal wire approaches the amorphous state, but the point is that this metal in no way can be described as being hard: it is nearly as soft as before the extrusion. That is the reason why we do not advance by sticking to the amorphous theory.

Robert J. Anderson and John T. Norton (authors' reply to discussion).—Notwithstanding that, in 1913, Dr. W. H. Hatfield demonstrated, that the idea of amorphous metal was a purely hypothetical proposition, and notwithstanding that no shred of experimental evidence has been produced to prove that amorphous metal actually exists, the discussion

* Director, Metallographic Institute of Stockholm.

of this paper shows that the amorphous-metal controversy is much alive. The authors do not intend to enter into any controversy about the matter; their object was to present certain new observed facts, which include the finding that the severely polished surface layer of metals gives a crystalline diffraction pattern.

The whole amorphous-metal hypothesis was reared on the concept that an amorphous film is produced on polishing, and the orthodox view is that metals are amorphized on cold work and that an amorphous cement exists between the grains of metals. There are no experimental facts in support of these views. The almost proverbial idea of amorphous metal is a result of the relentless insistence that because this concept nicely explains certain observed phenomena of metals therefore amorphous metal is a condition of actual fact. In all fairness, it must be admitted that much of our modern knowledge has resulted from the amorphous-metal hypothesis, but until the proponents of this bring forth actual experimental facts in support of their views it will have to be conceded, even by them, that amorphous metal is purely hypothetical.

True enough, the data presented in this paper do not prove conclusively that amorphous metal does not exist; but the fact remains that polished surfaces give crystalline diffraction patterns. No x-ray method apparently is capable of proving the non-existence of amorphous metal, and it was not the intention of the authors to convey the impression that such a method could do so. That the polished surface layer which gives the characteristic diffraction pattern is very thin is shown by the experiments with etched surfaces. The burden of proof for amorphous metal is on its proponents, not on those who disclaim its existence.

Mr. Yap suggests that a diffraction pattern could be secured from a layer of atoms (not arranged in any regular lattice spacing). If the atoms of an amorphous material were arranged in layers, the chances of obtaining a diffraction pattern would be very small, and the chance that this pattern of one line would check with that of the crystalline material would be very small indeed. It is not at all difficult to account for the uniform hardness of a polished surface without the aid of the amorphous-metal hypothesis; the uniformity of hardness is quite readily accounted for by the fineness of grain. The question of x-ray penetration is fully accounted for by the experiments with etched surfaces.

The authors did not touch on the question of amorphous cement, but so far as they can see there is no more sound reason for postulating amorphous cement than there is for postulating amorphization on cold work or polishing. Mr. Foley's ingenious explanation of grain boundaries serves in an eminently more satisfactory manner to explain intercrystalline fracture and the non-existence of amorphous cement than does the orthodox Rosenhain-Ewen explanation serve to explain its existence. The schematic block representation of grain-boundary conditions is untenable on an atomic basis.

Doctor Lester suggests that an amorphous layer, if such exists, would be seen in a general darkening of the photographic film; the authors found no such darkening, as was stated in the paper.

The authors were glad to have had the opportunity of making an independent check of Mr. Bain's work. His results and theirs show that the process of grain fragmentation seems to be the most important, if indeed not the only, process, operative on cold working. In Mr. Bain's crystallogram, the aluminum lines are quite strong, and it appears to the authors that their experiments with etched surfaces are much more conclusive. The authors varied the height of their polished surfaces in positions on the cassettes over a wide range with respect to the x-ray beam and made numerous experiments with the effect of etching for various periods of time on the resultant patterns. The experiments made with tilted surfaces are also germane to the point brought up by Mr. Bain, as are, too, those made with polished single crystals.

A device similar to the authors' unrestricted slit was used on Professor Bragg's original spectrometer, and similar devices have been used extensively ever since; the authors did not claim that their restricted slit was original.

The question of line intensity was dealt with in a paper by the authors, entitled The Crystal Structure of Cold-worked and Burnished Metals, read before the Physical Society at New York in February, 1925.

There can be no such things as molecules in crystalline metal; each atom is exactly equivalent to every other one, and the molecule conception may mean a few atoms or the number of atoms present in a ton, or any other quantity, of metal.

To sum up: The whole amorphous-metal hypothesis was reared on the concept that an amorphous layer is produced on polishing, and many futile experiments have been carried out to try to prove that this layer is amorphous. The general hypothesis served nicely to explain numerous observed facts regarding metals, but it is not necessary to assume (and is indeed highly improbable) that polished surfaces are amorphous, that amorphization occurs on cold working, or that amorphous cement exists at the grain boundaries of metals. The same facts regarding the phenomena exhibited by metals as have been explained by the amorphous conception can be more soundly explained on the basis of lattice strain, interatomic forces, and grain fragmentation. The most important conclusion that emerges from the present experiments is that the surface layer produced by polishing is crystalline. The authors are quite well aware that there conceivably can be amorphous metal present in this surface layer; their minds are entirely open on the question, and they are ready to acknowledge the existence of amorphous metal when it can be proved by experimental facts that this metal does exist.

Corrosion of Copper Alloys in Sea Water

By W. H. Bassett* and C. H. Davis,† Waterbury, Conn.

(New York Meeting, February, 1925)

The late J. P. Sparrow, chief operating engineer of the New York Edison Co., carried out a series of practical tests on condenser tubes of several copper alloys and reported on the results to the Association of Edison Illuminating Companies at its meeting in September, 1913. In the preparation of these tubes the senior author had the pleasure of coöperating. Copper-zinc alloys in the proportions of 60–40, 70–30, 80–20, 90–10, and Admiralty metal, which is in effect 70–30 with 1 per cent. of tin, were tried. Monel metal and several copper-nickel alloys, and 8, 5, and 3 per cent. aluminum bronze were also tried. At the time of this report, the aluminum bronze had been in service for 4½ years and seemed to be giving especially good results but later it began to fail and showed no substantial improvement over Admiralty metal. Monel metal was unsatisfactory and the nickel alloys apparently did not give better service than the Admiralty alloy.

Previous to the publication of the report, and after considerable discussion, it was agreed that a test where tubes of different kinds could be under laboratory observation would be advisable, so the apparatus described here was set up in The American Brass Co.'s Waterbury Laboratory. This was fitted with tubes of copper, brass, bronze, nickel silver, cupro-nickel and other alloys, and the test started on Oct. 11, 1912.

Salt water from East River, New York harbor, was barrelled and transported to the laboratory for the test. A fresh supply, completely replacing the water in service, was obtained at the end of each six months period.

Plan of Procedure

In general, the procedure was to inspect the tubes at short intervals and to remove those that had begun to leak. The tubes removed were carefully examined and a photographic and microscopic record of the

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character of the failure taken and placed upon file for assembling at the completion of the test. At the end of 10 years, a large proportion of the samples were, from all appearances, still in good condition. Considering this length of time sufficient for all of the alloys to have been acted upon to an extent that would clearly indicate their behavior, and as small test samples exposed in the same system had given positive results, the test was concluded.

After starting the test, it soon was found to be impractical to remove the tubes and to clean and determine the relative action of the salt water upon them; therefore small specimens of sheet metal, which could be weighed, were placed in the water. Alloys similar in composition to the tubes were chosen, specially annealed at different temperatures, and rolled to several degrees of hardness. This plan made possible a study of the effect of grain size and hardness on corrosion. These sheet-metal samples were weighed frequently and were carefully inspected and photographed.

The two phases of the investigation were, therefore, the attack of the sea water upon the walls of the tubes and the rate of solution of weighed samples in the same sea water. How closely the two methods of procedure gave similar conclusions is shown in the summary of results.

Accelerated Corrosion Tests

The sea-water tests have extended over a period of 10 years, involving time and effort that cannot ordinarily be allotted to a single problem. Various accelerated corrosion tests had previously been run, with the idea of determining the relative corrodibility of alloys but without concordant results. Recently, the salt-spray corrosion test has been developed and used with such consistent success that it is possible to make a direct comparison between the 10-year sea-water tests and the accelerated salt-spray tests of a few months duration. It is gratifying that the several lines of attack have produced results closely in harmony.

Apparatus

Arrangement of Tubes

The situation and general plan of the apparatus are shown in Fig. 1. This view was taken at the end of the 10-year period with the head of an upper tank removed to show the position of the tubes that failed. The other ends of the 8-ft. tubes were similarly packed in the head of another tank in the rear. The sea water from the large reservoir below was pumped to the rear tank by a small rotary pump, flowed through the tubes to the tank shown, and overflowed down the vertical pipe in the center, completing the circuit. The tank was built of wood, coated with asphalt paint thoroughly dried, and had no iron

exposed to the salt water. The tubes were packed in the heads with paraffined wick. This allowed moisture to penetrate the head about the tubes and caused a serious attack upon some of them where the ends were enclosed in the wood. Failures occurring for this reason have been left out of consideration in the summing up of the results. The water used for this experiment was taken every six months, in April and October, from the East River, New York harbor; approximately eighteen barrels was used to fill the tanks.

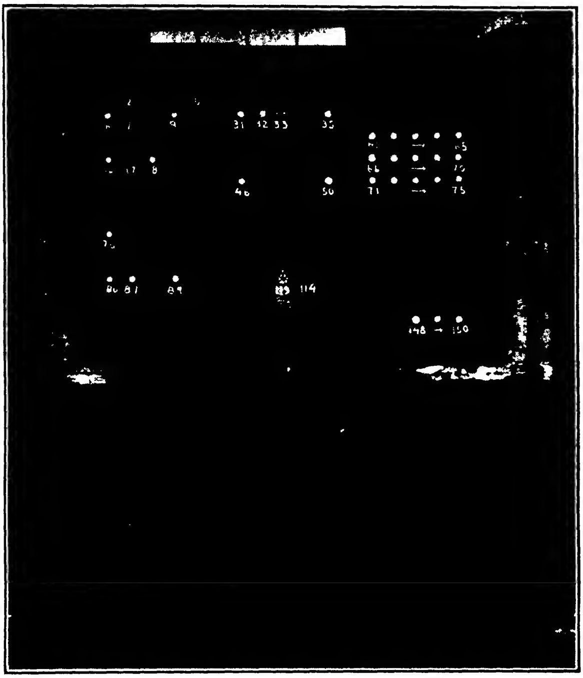


Fig. 1.—One upper tank with head removed to show location of tubes failing in less than 10 yr.; sea water traveled from a similar tank at farther end, overflowed down vertical pipe to reservoir below, and was repumped through system. Tubes 2, 5, copper, failed at head only; 6, 7, 9, gilding (7 was replaced by a new brass tube 7*a*); 16, 17, 18, rich low brass (17 failed at 10 yr.); 31, 32, 33, 35, Muntz metal (60–40 Cu-Zn); 46, 50, brass with tinned surface; 61 to 65, Muntz metal; 66 to 75, Muntz metal with tinned surface; 76, brass (66.25 per cent. Cu, 0.50 per cent. Pb); 86, 87, gilding; 89, bronze (81 per cent. Cu, 18 per cent. Zn, 1.00 per cent. Sn); 113, 114, 148, 149, 150, 8 per cent. aluminum bronze.

Location and Arrangement of Sheet-metal Specimens

The strips of sheet metal were drilled at one end and were suspended from glass rods, the ends of which were fixed in a wooden frame, as shown in Fig. 2. This entire arrangement was totally immersed in the sea water in the large reservoir underneath the tube specimens. The accelerated,

or salt-spray, tests were conducted in another laboratory and by a different operator; these will be described later.

It was originally planned to heat the water in the tanks but this was impractical on account of evaporation. The test, therefore, was conducted at room temperature; that is, from 18° C. to 23° C. The salt water was analyzed both before and after its six-months' use; representative analyses are given in Table 1.

As the water evaporated its concentration and gravity were regulated by the addition of fresh water from city mains. When received, the sea water was sometimes very dirty and fermenting. After it was pumped through the tank for two or three days, aeration clarified it. Organic

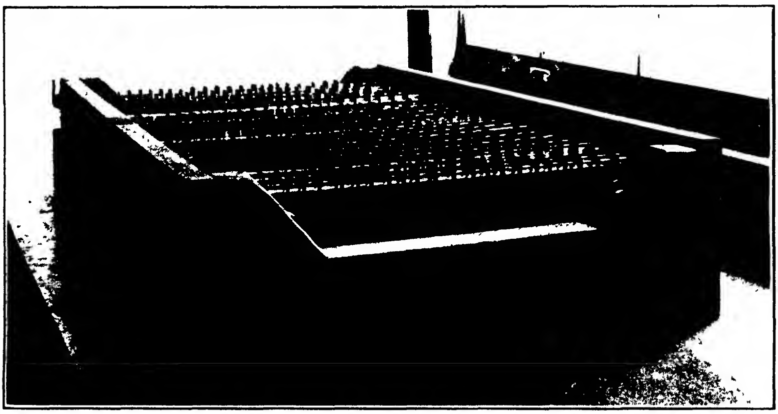


FIG. 2.—APPARATUS FOR HOLDING SPECIMENS; A COPPER-FASTENED WOODEN FRAME SUPPORTING GLASS RODS THAT PASS THROUGH HOLES IN THE SPECIMENS.

matter present apparently became oxidized, or settled to the bottom of the larger reservoir, so that the water entering the tubes was clear and clean during most of the period of testing.

CONDENSER TUBE SPECIMENS IN SALT WATER

Tube Alloys and Methods of Manufacture

Complete analyses were made of those samples that failed in less than 10 years and also of one of each group of the five tubes representing a particular alloy or condition; the annealed and the hard-drawn tube samples are about equal in number. Those that were tinned were confined to the 72–28 and the 61½–38½ copper-zinc alloys. In no case was the finishing draft on the tubes severe, the greatest reduction being approximately equivalent to 15 per cent. in the thickness of the wall.

Wherever possible, the tubes were taken from mill stock manufactured according to the standard methods prevailing at the time. Alloys were included, however, that are not ordinarily used for tubes—manganese

TABLE 1.—*Composition of East River Water*

	Old Water after 155 days, Mar 18, 1913, No. 1184		New Water, Mar. 18, 1913, No. 1185		Old Water, Aug 24, 1914, No 20530		New Water, Aug. 22, 1914, No. 20527		New Water, Aug., 1921, No. 25489		Atlantic Ocean Water[a] from 20° 54′ N., 40° 44′ W.	
	Parts per Million	Grains per U. S. Gal.	Parts per Million	Grains per U. S. Gal.	Parts per Million	Grains per U. S Gal.	Parts per Million	Grains per U. S. Gal.	Parts per Million	Grains per U. S. Gal.	Parts per Million	Grains per U. S. Gal.
Total residue.... ...	21,303	1,242.3	26,614	1,552 1	18,014	1,050	27,176	1,583.0	21,500	1,255		
Fixed residue... .	17,870	1,042.1	22,928	1,337.2	15,870	930	22,761	1,326.0			34,700	2,020
Ignition loss..	3,433	200.2	3,686	214 9	2,144	125	4,415	257.5				
$Fe_2O_3 + Al_2O_3$. ..					19.7	1 1	28	1.64				
CaO... . . .	467.0	27.3	366.7	21.39	457.1	26 6	788	46.0	495.0	28.8	657	38.3
MgO...	1,098.0	64.0	856	49.92	1,170	68 2	1,268	74.0	956.0	55.7	2,120	124
Na_2O. . . .					13,933	812	22,618	1,320	9,460	553	14,110	822
K_2O. .. .									252.0	14.7	870	50.7
Cl...	10,560	615.9	12,993	757.8	8,850	516	13,471	785 0	11,000	642	19,012	1,110
SO_3.. . .	1,277	74.5	1,542	89.9	1,410	82 2	1,687	98 0	1,305	76	1,783	104
NH_3..	90	5.3	52	3.0	111.9	6 5	52 1	3 0				
Cu.......	3.0	0.18			10.8	0.6						
Specific gravity, 60° F..	1.018				1.015		1 021		1.012			
Oxygen required to oxidize organic matter...									22			

[a] Bibra, Annalen, 77, 90.

TABLE 2.—*Results of Tests*

	Tube No.	Composition									Time Immersed			Nature of Corrosion
		Per Cent. Copper	Per Cent. Zinc	Per Cent. Lead	Per Cent. Iron	Per Cent. Tin	Per Cent. Man-ganese	Per Cent. Alumi-num	Per Cent. Nickel	Per Cent. Arsenic	Years	Months	Days	
Copper, hard.	1	99.98									10			Corrosion occurs by slight irregular solution 0.003 in. deep. Deepest of the few pits is about 0.013 in. The two apparent failures were due to corrosion in wooden head of apparatus.
	2*	99.906									9		19	
	3	99.930									10			
	4	99.80									10			
	5*	99.909									9		19	
Gilding, annealed....	6*	94.44	5 52	0.02	0.02						9		19	Even solution from 0.002 to 0.004 in., but many fine pits, often in streaks, in all samples. Average pit was 0.015 in. deep, but three failures resulted from pits through wall. Tube No. 7 was replaced with a brass tube No. 7*a*.
	7*	94.36	5.60	0 01	0 03							10	28	
	8	94.41	5.56	0 01	0 02						10			
	9*	94.45	5.50	0.02	0 03						2	3	9	
	10	94.34	5.66								10			
Commercial bronze, hard.	11	89.96	9.98	0.02	0 04						10			Dissolved evenly about 0.002 in., but a few shallow streaked areas were dissolved to 0.015 in. Tubes generally in good condition.
	12	90 02	9.98								10			
	13	89.87	10 20								10			
	14	90 00	10.00								10			
	15	90.03	9.97								10			
Rich low brass, annealed.	16*	84 89	15.05	0.03	0 03						9		19	General solution was 0.002 in There were pinhole pits, also pits averaging 0.010 to 0.025 in. in three tubes that failed.
	17*	85.19	14.73	0.04	0 04						10			
	18*	85.10	14.86	0.01	0.03						2	10	24	
	19	84.88	15.12								10			
	20	85.02	14 98								10			
Low brass, hard......	21	79 87	20 13								10			Slightly and evenly dissolved about 0.002 in. with a few small depressions 0.005 in. All tubes were in very fine condition.
	22	79.97	19.96	0.04	0.03						10			
	23	79.82	20.18								10			
	24	79 85	20.15								10			
	25	79.95	20.00								10			

Brass, hard..	26	75 03	24 93	0.01	0.03						10			Evenly dissolved about 0.003 in., but with some depressions 0.018 in. No dezinkification, and tubes were in good condition.
	27	75.04	24 96								10			
	28	75.48	24.52								10			
	29	75.24	24 76								10			
	30	75.22	24.78								10			
Muntz, annealed	31*	61.12	38.77	0 10	0 01						1	1	8	All tubes were dezinkified through, causing early failure. Tube No. 34 was riddled with dezinkified areas though it did not leak. Unaffected surface was dissolved not more than 0.003 in.
	32*	61.46	38.35	0.17	0 02						1	8	4	
	33*	61.58	38.29	0.11	0 02						1	8	4	
	34	63.11	36.71	0.16	0 02						10			
	35*	61.14	38 72	0 11	0 03						1	1		
Brass, tinned, hard	36	71 19	28.74	0 03	0 04						10			Badly dezinkified under tinned inner surface over practically entire tube to depth of 0.015 in. and to 0.025 in. Attack was in areas rather than in pits.
	37	71.26	28 74								10			
	38	71.61	28 39								10			
	39	71.08	28.92								10			
	40	70.97	29.03								10			
Brass, annealed	41	68.77	31 23								10			None were dezinkified but one was badly pitted to a maximum depth of 0.027 in. Generally speaking, solution was only 0 003 in. and tubes were in fine condition.
	42	71.26	28.74								10			
	43	70 04	29 90	0.04	0 02						10			
	44	71 03	28.97								10			
	45	71.15	28.85								10			
Brass, tinned hard.	46*	71 06	28 87	0.05	0 02						4	9		Were not dezinkified but were dissolved in sharp streaked depressions penetrating wall in two cases. Average depth of depressions was 0.010 in.; elsewhere metal was protected by tin or dissolved 0.003 in.
	47	70.75	29 19	0.04	0 02						10			
	48	69.11	30 89								10			
	49	70.24	29 76								10			
	50*	70.78	29 14	0 06	0.02						2	10	28	
Brass, annealed	51	66.62	33.31	0.03	0 04						10			Generally dezinkified in areas and spots to depth of 0.025 in.; no failures.
	52	66.72	33.28								10			
	53	66.78	33.22								10			
	54	66.57	33.43								10			
	55	66.51	33.49								10			
Common brass, annealed.	56	65.86	33.97	0.13	0.04						10			Generally but not totally dezinkified 0.010 in.; also in pits practically through wall.
	57	67.78	32.22								10			
	58	66.87	33.13								10			
	59	66.07	33.93								10			
	60	66.46	33.54								10			

* Tube failed in less than 10 yr.

TABLE 2.—*Continued*

	Tube No.	Composition									Time Immersed			Nature of Corrosion
		Per Cent. Copper	Per Cent. Zinc	Per Cent. Lead	Per Cent. Iron	Per Cent. Tin	Per Cent. Manganese	Per Cent. Aluminum	Per Cent. Nickel	Per Cent. Arsenic	Years	Months	Days	
Muntz, hard.........	61*	61.79	38.12	0.11	0.03						1	1		Broad dezinkified pits under heavy scale on upper inner side causing failure. Slight general dezinkification.
	62*	62.17	37.71	0.09	0.03						1	1		
	63*	61.69	38.18	0.10	0.03						1	1		
	64*	61.00	38.83	0.13	0.04						1	1		
	65*	61.12	38.74	0.11	0.03						1	1		
Muntz, tinned.......	66*	62.19	37.67	0.12	0.02						1	8	4	Hard. All failures by dezinkification in spots through tin.
	67*	61.95	37.91	0.12	0.02						1	8	4	Hard
	68*	61.97	37.89	0.12	0.02						1	8	4	Hard
	69*	61.60	38.16	0.17	0.07						1	8	4	Annealed
	70*	61.67	38.16	0.10	0.07						1	8	4	Annealed
Muntz, tinned, annealed.	71*	61.82	38.03	0.13	0.02						2	2	4	All failures by dezinkification in spots through tin on inner surface.
	72*	61.55	38.35	0.08	0.02						1	1		
	73*	61.82	37.98	0.18	0.02						2	2	4	
	74*	61.78	38.05	0.15	0.02						2	2	4	
	75*	61.26	38.61	0.10	0.03						1	1		
Leaded brass, hard...	76*	66.28	33.11	0.55	0.03					0.0263	3	9	17	Tube containing arsenic showed intergranular corrosion. General solution on this and remaining tubes was only 0.003 in. Tubes without arsenic were not dezinkified but remained in good condition.
	77	65.97									10			
	78	66.40	32.89	0.69	0.02						10			
	79	66.03									10			
	80	67.54									10			
Bronze, hard.........	81	94.45				5.19					10			Generally dissolved about 0.003 in. but a few spots were 0.015 in. deep.
	82	94.44		0.02	0.07	5.04					10			
	83	94.39				5.19					10			
	84	94.39				5.16					10			
	85	94.50				5.23					10			
Gilding, annealed....	86*	94.23	5.74	0.01	0.02						2	10	24	Badly pitted in small and large holes over much of tubes, especially at top. Faliure due to pitting.
	87*	94.35	5.57	0.02	0.06						1	8	4	

Bronze, annealed.....	88	81.30	17.79	0.02	0.02	0.87					10			Not dezinkified but thinned irregularly 0.010 ± in. One tube failed by solution of oval areas ½ in. wide and ½ to 1 in. long.
	89*	81.32	17.79	0.02	0.03	0.84					2	3	4	
	90	81.54	17.61			0.85					10			
Bronze, hard...	91	92.32	7.17	0.02	0.02	0.47					10			These were evenly dissolved 0.003 in. but an occasional shallow depression was 0.016 in. deep. Generally in good condition.
	92	92.30	7.14			0 56					10			
	93	92.16	7.31			0.53					10			
	94	92.11	7.32			0.57					10			
	95	92.15	7.26			0.59					10			
Admiralty, annealed	96	70.62	28.25			1.13					10			No dezinkification but slight solution or etching 0.002 in. Occasionally a depression 0.005 in.
	97	70.54	28.32	0.03	0.02	1 09					10			
	98	70.73	28.28			0.99					10			
	99	70.58	28.34			1.08					10			
	100	70.72	28.15			1.13					10			
Manganese bronze, hard.	101	59.27				0.69					10			Practically entire inner surface dezinkified to 0.015 in. Many spots penetrated wall though no leaking had been noticed.
	102	58.87				0.64					10			
	103	59.10				0.61					10			
	104	58.70	39.22	0.012	1.02	0.52	0.53				10			
	105	58.73				0.43					10			
Tobin bronze.	106	63.19	36.24			0.57					10			Annealed — Not dezinkified, but some slight solution in streaks 0.001 to 0.003 in. There was no pitting. Tubes were in good condition.
	107	63.42	36.00			0.58					10			Hard
	108	64 44	34.99			0.57					10			Hard
	109	65.07	34.43			0.50					10			Annealed
	110	62.95	36.38	0.10	0.03	0.54					10			Annealed
Aluminum bronze, hard........... ...	111	92.30						7.70			10			Deep broad pitting occurs over much of surface to to depth of 0.025 in. Almost no solution except at pits.
	112	92.34						7.66			10			
	113*	92.14	0.00					7.70			2	3	4	
	114*	92.15	0.00	0.002	0.03			7.80	0.005		10			
	115	92.30						7.70			10			
Bronze, hard.........	116	92.23				7.46					10			Dissolved in a few broad deep rolling areas, in some places depth of 0.033 in. General solution was only to depth of 0.006 in.
	117	91.60				8.59					10			
	118	92.23				7.61					10			
	119	92.00	0.00	0.02	0.11	7.55			0.012		10			
	120	91.64				7.84					10			
Cupro-nickel, hard...	121	74.98	0.00	0.010	0.10		0.29		24.62		10			Evenly dissolved 0.002 in., but with a number of broad smooth shallow areas 0.020 in. deep. Of good appearance generally.
	122	74.75	0.00						25.25		10			
	123	74.75	0.00						25.27		10			
	124	74.77	0.00						25.23		10			
	125	73.96	0.00						26.04		10			

* Tube failed in less than 10 yr.

TABLE 2.—*Continued*

	Tube No.	Composition: Per Cent. Copper	Per Cent. Zinc	Per Cent. Lead	Per Cent. Iron	Per Cent. Tin	Per Cent. Manganese	Per Cent. Aluminum	Per Cent. Nickel	Per Cent. Arsenic	Time Immersed: Years	Months	Days	Nature of Corrosion
Cupro-nickel, hard...	126	83.59	0.00						16.41		10			Very smooth and evenly dissolved about 0.003 in. with some areas 0.005 in. deep. Of good appearance generally.
	127	84.29	0.00						15.71		10			
	128	84.25	0.00						15.75		10			
	129	82.93	0.00						17.07		10			
	130	85.08	0.00	0 01	0.10		0 14		14.67		10			
Nickel silver, hard .	131	56.95	27.74						15.31		10			Slight solution 0.002 in. and deep etching on one sample only. Deeper points were only 0.005 in. deep so that appearance and condition of tubes was excellent.
	132	57.04	27.72						15.24		10			
	133	57.15	27.80	0.038	0.12		0.16		14.73		10			
	134	57.05	27.78						15.17		10			
	135	57.11	27.49						15.40		10			
Cupro-nickel, hard. .	136	89.16	0.96						9 88		10			Slightly dissolved 0.003 in. with isolated pits 0.020 in. deep in one tube. Remaining tubes had fine appearance.
	137	89.13	0 00						10.87		10			
	138	89.21	0.00	0 010	0.18		0.41		10 19		10			
	139	89.08	0.00						10 92		10			
	140	89.17	1.02						9.81		10			
Aluminum bronze, hard.	141	95.00	0.00	0 003	0 03			4 95	0.005		10			Although these did not fail, they were generally pitted over much of surface to an average depth of 0.010 to 0.025 in. Many of pits were practically through tube wall.
	142	94.80						5.20			10			
	143	94.76						5.24			10			
	144	94.92						5 08			10			
	145	94.82						5.18			10			
Aluminum bronze ...	146	92.41	0.00	0.003	0.04			7.53	0 010		10			Hard } Broad deep pits in all tubes resulting in three failures. Average depth of pit was 0.025 in.
	147	92.20	0.00					7.75			4			Hard
	148*	92.46	0.00					7 38			3	6	22	Hard
	149*	91.62						8 38			10			Hard
	150*	92.27						7.73			2	2	4	Annealed
Brass, hard	7a Replacement	71.23	28.71	0.02	0.04						9	1		Dezinkified generally in streaks about 0.006 in. No pitting.

* Tube failed in less than 10 yr.

and other bronzes, for instance. All the tubes were 1-in. outside diameter, 0.049-in. gage (No. 18 Stubbs) and 8 ft. long. Five pieces, alike in composition and temper, were used in order that a fair average of the behavior of the alloy might be found. It was well that several samples of each were taken, for some of the alloys were erratic in their behavior.

Sheet-metal Specimens in Sea Water

The sheet-metal specimens were purposely selected to have the approximate composition of the tubes in order that direct comparisons might be made and data from one test applied to the other.

Preparation of Specimens

Strips were first finished with a 60.4 per cent. reduction (8 B. & S. numbers) by cold rolling to 0.051 in. thick, and were slit to 1 in. in width. One set of these hard samples was held in this condition, but the others were annealed at 450°, 550°, 650°, and 750° C. One set each of these annealed pieces was held but the remaining sets were rolled again to complete the schedule outlined below.

Different Specimens Were Annealed at, Degrees C	Then Reduced by Rolling, Per Cent.	As Expressed in B. & S. Nos. Hard	Final Gage, Inches
450, 550, 650, and 750.	0	0 soft	0.051
450, 550, 650, and 750.	10.9	1 number, hard	0.045
450, 550, 650, and 750.	20.7	2 numbers, hard	0.040
450, 550, 650, and 750.	37.1	4 numbers, hard	0.032
450, 550, 650, and 750.	50.0	6 numbers, hard	0.025
Mill anneal 600±	60.4	8 numbers, hard	0.051

There were, therefore, twenty-one samples of each alloy, four in the annealed condition, four each rolled 1, 2, 4, and 6 B. & S. numbers and one each rolled 8 B. & S. numbers hard. The total surface area of the 21 samples was 215.3 sq. in. The total surface areas of the individual specimens were:

Annealed	11.49 sq. in.
1 number, hard	9.99 sq. in.
2 numbers, hard	9.89 sq. in.
4 numbers, hard	9.83 sq. in.
6 numbers, hard	9.75 sq. in.
8 numbers, hard	11.49 sq. in.

TABLE 3.—*Analyses of Sheet Metal for Corrosion Tests in Sea Water*

Mark	Alloy	Per Cent. Copper	Per Cent. Zinc	Per Cent. Nickel	Per Cent. Lead	Per Cent. Iron	Per Cent. Tin	Per Cent. Manganese	Per Cent. Aluminum	Per Cent. Phosphorus
A	Copper....................	99.943								
B	Gilding....................	96.91	3.06		0.01	0.02				
M	Gilding....................	94.90	5.07		0.02	0.01				
Q	Commercial bronze.........	89.93	10.02		0.02	0.03				
Z	Low brass.................	80.07	19.86		0.05	0.02				
V	Brass.....................	72.45	27.47		0.06	0.02				
T	Brass.....................	66.11	33.83		0.04	0.02				
O	Brass.....................	66.20	33.65		0.13	0.02				
E	Brass.....................	63.32	36.50		0.15	0.03				
D	Brass.....................	61.79	38.06		0.13	0.02				
C	Muntz.....................	60.49	39.29		0.15	0.07				
S	Leaded brass..............	67.29	31.99		0.69	0.03				
J	Bronze....................	94.72	0.22				5.00			
R	Bronze....................	91.30	0.14				8.44			
N	Bronze....................	92.73	6.54		0.02	0.06	0.65			
X	Low brass.................	80.84	18.08		0.07	0.06	0.95			
W	Admiralty.................	69.72	28.92		0.03	0.04	1.29			
P	Tobin bronze..............	61.31	37.72		0.06	0.04	0.87			
H	Cupro-nickel..............	75.46	0.00	24.12		0.15		0.27		
I	Cupro-nickel..............	79.89	0.00	19.88		0.09		0.14		
G	Cupro-nickel..............	84.75	0.00	14.99		0.12		0.14		
U	Nickel-silver.............	57.42	26.71	15.51		0.23		0.12		
K	Cupro-nickel..............	89.27	0.00	10.35		0.15		0.23		
Y	Aluminum bronze...........	95.14	0.00						4.86	
L	Phosphor bronze...........	95.72	0.00				4.09			0.29
F	Aluminum bronze...........	92.24	0.00						7.76	

The "Mark" indicates alphabetically the order of greatest loss; copper losing most and low brass least; see Table 4.

TABLE 4.—*Corrosion of Copper Alloys in Sea Water (21 Samples Including Rolled and Annealed Material of Each Alloy; Total Area Exposed, 215.3 Sq. In.)*

Period.......	0–2 Months	2–4 Months	4–6 Months	6–10 Months	10–16 Months	16–39 Months	39–62 Months	62–98 Months	Total Loss, Grams per Square Inch
Mark	Loss in Weight for Eight Consecutive Periods, in Grams per Square Inch per Month								
A	0.00719	0.00274	0.00301	0.00051	0.01393	0 00181	0.00325	0.00065	0.03309
B	0.00654	0.00218	0.00102	0.00023	0.01147	0.00143	0.00339	0.00065	0.02691
C	0.00167	0.00315	0.00334	0.00181	0.01096	0.00148	0.00264	0.00125	0.02630
D	0 00329	0.00376	0 00241	0 00176	0.00887	0.00153	0.00311	0.00111	0.02584
E	0.00459	0.00315	0.00227	0.00139	0.00766	0.00176	0.00315	0.00125	0.02522
F	0.00000	0.00013	0.00079	0.00037	0.01272	0.00385	0.00571	0.00065	0.02422
G	0 00594	0 00106	0.00074	0.00037	0.00998	0.00125	0.00301	0.00111	0.02346
H	0 00473	0 00143	0.00125	0.00037	0.01091	0.00106	0.00236	0.00106	0.02317
I	0.00469	0.00148	0.00097	0.00037	0.01086	0.00102	0 00278	0.00092	0.02309
J	0.00673	0.00102	0.00013	0.00023	0.00984	0.00153	0.00264	0.00055	0.02267
K	0 00654	0.00078	0 00032	0.00023	0.00859	0 00162	0 00325	0 00102	0.02235
L	0.00599	0.00143	0.00092	0 00027	0.00863	0 00167	0.00260	0.00065	0.02216
M	0 00640	0.00246	0.00102	0 00027	0.00719	0 00106	0.00264	0.00051	0.02155
N	0.00575	0.00176	0 00060	0.00023	0 00808	0.00106	0 00246	0.00055	0 02049
O	0 00566	0.00143	0 00060	0.00037	0 00227	0.00167	0.00297	0.00213	0.01710
P	0.00455	0 00125	0.00032	0 00032	0.00343	0 00157	0.00325	0 00176	0.01645
Q	0.00575	0.00190	0.00074	0 00023	0.00492	0 00088	0.00134	0.00069	0.01645
R	0.00580	0.00051	0 00023	0.00023	0 00636	0 00078	0.00199	0 00046	0.01636
S	0.00464	0.00148	0.00065	0.00037	0 00264	0 00139	0.00260	0.00176	0.01553
T	0.00557	0.00134	0.00041	0 00027	0.00213	0.00111	0.00250	0.00130	0.01463
U	0 00334	0 00241	0.00116	0.00032	0 00399	0 00069	0.00176	0.00069	0.01436
V	0.00524	0.00120	0.00069	0.00032	0 00227	0.00078	0.00227	0.00097	0.01374
W	0.00464	0.00120	0.00023	9 00023	0 00250	0.00083	0.00213	0.00195	0.01371
X	0.00557	0.00097	0.00018	0.00018	0 00399	0.00055	0.00130	0.00083	0.01357
Y	0.00018	0.00009	0.00037	0.00032	0.00975	0 00134	0.00116	0.00023	0.01344
Z	0 00464	0 00143	0.00046	0.00027	0 00292	0.00055	0.00139	0.00083	0.01249

NOTE.—The letters indicate the alloys whose compositions are given in Table 3. These data have been used to prepare Figs. 8 to 10, inclusive.

TABLE 5.—*Corrosion of Copper Alloys in Sea Water*

	Total Loss of Each Sample in 8½ Yr., Expressed as Grams Lost per Square Inch of Surface Exposed						
Per cent. copper	99.943	97	95	90	80	72	66.6
Per cent. zinc		3	5	10	20	28	33 3
8 numbers hard	0.0151	0.0170	0.0097	0 0081	0.0068	0.0073	0.0086
750° C.							
Annealed	0.0136	0.0105	0.0084	0.0056	0 0057	0.0057	0.0068
1 number hard	0.0104	0.0099	0.0072	0 0072	0 0049	0.0053	0.0068
2 numbers hard	0.0095	0.0097	0.0071	0 0055	0 0046	0.0066	0.0074
4 numbers hard	0 0148	0.0092	0.0088	0 0054	0 0054	0.0066	0.0077
6 numbers hard	0.0152	0.0110	0.0062	0.0066	0 0056	0.0069	0.0082
650° C.							
Annealed	0.0156	0.0084	0.0066	0 0056	0 0051	0.0059	0.0076
1 number hard	0.0107	0.0083	0.0058	0 0054	0 0050	0.0054	0.0061
2 numbers hard	0.0086	0.0078	0.0054	0.0045	0 0044	0.0058	0.0064
4 numbers hard	0 0144	0.0074	0.0123	0 0058	0 0055	0 0072	0.0083
6 numbers hard	0 0129	0.0136	0.0079	0 0063	0.0047	0 0064	0.0083
550° C.							
Annealed	0.0105	0.0113	0 0068	0 0058	0 0051	0.0059	0 0080
1 number hard	0.0110	0.0119	0.0089	0.0051	0 0046	0 0057	0.0064
2 numbers hard	0 0101	0 0117	0.0056	0.0059	0.0051	0.0067	0 0072
4 numbers hard	0 0112	0.0119	0 0078	0.0054	0 0045	0 0063	0.0074
6 numbers hard	0.0116	0 0118	0.0104	0.0066	0.0049	0 0067	0.0087
450° C.							
Annealed	0 0122	0.0089	0 0073	0.0059	0.0050	0.0064	0.0079
1 number hard	0 0112	0.0104	0 0094	0.0062	0.0052	0.0066	0.0071
2 numbers hard	0.0106	0.0107	0.0069	0.0052	0 0048	0 0070	0.0074
4 numbers hard	0.0116	0.0123	0.0119	0 0060	0 0053	0.0070	0.0083
6 numbers hard	0 0087	0.0100	0 0077	0 0059	0 0046	0 0066	0.0077
Total	0 2495	0 2237	0 1681	0.1240	0 1068	0.1340	0.1583

Per cent. copper	65	63	61 5	60	66 25	95	92
Per cent. zinc	35	37	38.5	40	33.25		
Per cent. tin						5	8
Per cent. lead					0.5		
8 numbers hard	0.0087	0.0109	0.0116	0.0108	0.0096	0.0099	0.0064
750° C.							
Anneal	0.0117	0.0090	0.0091	0.0104	0 0088	0.0107	0.0090
1 number hard	0.0117	0.0089	0.0088	0.0092	0 0051	0.0094	0 0058
2 numbers hard	0.0120	0.0097	0 0101	0 0106	0 0078	0.0092	0.0049
4 numbers hard	0.0085	0.0098	0.0098	0.0091	0 0115	0.0080	0.0052
6 numbers hard	0.0093	0.0104	0.0110	0.0097	0.0094	0.0068	0.0049
650° C.							
Anneal	0.0132	0.0140	0.0109	0.0110	0.0088	0.0110	0.0074
1 number hard	0.0121	0.0116	0.0092	0.0098	0 0066	0.0098	0.0057
2 numbers hard	0.0117	0.0104	0.0099	0.0107	0 0098	0.0087	0.0056
4 numbers hard	0 0089	0.0108	0.0111	0.0121	0 0074	0.0087	0.0052
6 numbers hard	0.0094	0.0101	0.0111	0.0089	0.0089	0.0086	0.0049
550° C.							
Anneal	0.0121	0.0125	0 0123	0.0124	0.0091	0.0108	0.0102
1 number hard	0.0108	0.0119	0.0105	0.0102	0.0101	0.0089	0.0063
2 numbers hard	0.0088	0.0113	0.0107	0.0113	0.0111	0.0079	0.0049
4 numbers hard	0.0091	0.0103	0.0108	0.0112	0.0106	0.0086	0.0054
6 numbers hard	0.0095	0.0128	0.0132	0.0115	0.0085	0.0089	0.0076
450° C.							
Anneal	0.0107	0.0116	0.0109	0.0117	0.0054	0.0108	0.0086
1 number hard	0.0086	0.0111	0.0118	0.0109	0.0115	0.0095	0.0078
2 numbers hard	0.0090	0.0108	0.0114	0.0146	0.0091	0.0081	0.0059
4 numbers hard	0.0095	0.0120	0.0114	0.0120	0.0086	0.0089	0.0064
6 numbers hard	0.0092	0.0105	0.0110	0.0108	0.0081	0.0088	0.0050
Total	0.2145	0.2304	0.2266	0.2289	0.1858	0.1920	0.1331

TABLE 5.—*Continued*

	Total Loss of Each Sample in 8½ Yr., Expressed as Grams Lost per Square Inch of Surface Exposed						
Per cent. copper..	93.0	81	70	60.00	75	80	85
Per cent. zinc....	6.5	18	29	39.25			
Per cent. tin ..	0.5	1	1	0.75			
Per cent. nickel...					25	20	15
8 numbers hard	0.0075	0.0052	0.0080	0.0095	0.0102	0.0093	0.0113
750° C.							
Anneal	0.0105	0.0061	0.0057	0.0116	0.0103	0.0109	0.0115
1 number hard	0.0082	0.0049	0.0047	0.0100	0.0091	0.0091	0.0106
2 numbers hard	0.0073	0.0055	0.0071	0.0094	0.0096	0.0094	0.0106
4 numbers hard	0.0058	0.0048	0.0123	0.0108	0.0087	0.0093	0.0101
6 numbers hard	0.0070	0.0057	0.0096	0.0093	0.0089	0.0091	0.0099
650° C.							
Anneal	0.0075	0.0057	0.0090	0.0155	0.0106	0.0105	0.0115
1 number hard..	0.0055	0.0049	0.0049	0.0130	0.0091	0.0095	0.0099
2 numbers hard	0.0066	0.0049	0.0053	0.0085	0.0097	0.0101	0.0098
4 numbers hard	0.0066	0.0050	0.0074	0.0086	0.0096	0.0097	0.0108
6 numbers hard	0.0056	0.0050	0.0090	0.0097	0.0090	0.0093	0.0099
550° C.							
Anneal..	0.0111	0.0064	0.0100	0.0125	0.0118	0.0109	0.0113
1 number hard	0.0086	0.0048	0.0055	0.0087	0.0092	0.0098	0.0102
2 numbers hard	0.0074	0.0049	0.0125	0.0072	0.0091	0.0095	0.0098
4 numbers hard	0.0083	0.0047	0.0062	0.0103	0.0092	0.0091	0.0091
6 numbers hard	0.0108	0.0056	0.0096	0.0091	0.0089	0.0088	0.0086
450° C							
Anneal	0.0099	0.0053	0.0059	0.0090	0.0104	0.0110	0.0112
1 number hard	0.0089	0.0051	0.0078	0.0084	0.0100	0.0094	0.0092
2 numbers hard	0.0075	0.0051	0.0101	0.0094	0.0090	0.0089	0.0109
4 numbers hard	0.0087	0.0048	0.0091	0.0088	0.0098	0.0098	0.0102
6 numbers hard	0.0087	0.0064	0.0079	0.0092	0.0089	0.0092	0.0095
Total . .	0.1680	0.1108	0.1676	0.2085	0.2011	0.2026	0.2159

Per cent. copper ..	56.66	90	95	95.5	92		
Per cent. zinc	28.33						
Per cent. nickel	15.00	10					
Per cent. aluminum..			5		8		
Per cent tin				4.5			
Per cent. phosphorus .				0.5			
8 numbers hard.	0.0057	0.0108	0.0054	0.0059	0.0187		0.2480
750° C							
Anneal	0.0061	0.0109	0.0038	0.0116	0.0200		0.2440
1 number hard ..	0.0048	0.0098	0.0063	0.0102	0.0152		0.2135
2 numbers hard..	0.0053	0.0099	0.0060	0.0098	0.0183		0.2229
4 numbers hard..	0.0049	0.0098	0.0063	0.0082	0.0151		0.2259
6 numbers hard	0.0059	0.0096	0.0064	0.0094	0.0146		0.2266
650° C.							
Anneal.........	0.0065	0.0102	0.0067	0.0103	0.0174		0.2525
1 number hard .	0.0050	0.0109	0.0055	0.0078	0.0150		0.2125
2 numbers hard..	0.0053	0.0103	0.0077	0.0094	0.0173		0.2146
4 numbers hard...	0.0059	0.0105	0.0079	0.0061	0.0156		0.2288
6 numbers hard..	0.0055	0.0098	0.0070	0.0085	0.0149		0.2252
550° C.							
Anneal.............	0.0085	0.0127	0.0052	0.0118	0.0171		0.2621
1 number hard...	0.0060	0.0106	0.0044	0.0092	0.0160		0.2253
2 numbers hard..	0.0055	0.0095	0.0041	0.0094	0.0148		0.2220
4 numbers hard..	0.0063	0.0109	0.0065	0.0088	0.0137		0.2236
6 numbers hard...	0.0061	0.0099	0.0054	0.0085	0.0107		0.2347
450° C.							
Anneal....................	0.0067	0.0114	0.0052	0.0103	0.0177		0.2373
1 number hard..	0.0051	0.0097	0.0075	0.0096	0.0148		0.2328
2 numbers hard.... ...	0.0052	0.0094	0.0051	0.0090	0.0140		0.2251
4 numbers hard............	0.0058	0.0100	0.0059	0.0092	0.0123		0.2356
6 numbers hard..	0.0056	0.0102	0.0082	0.0086	0.0093		0.2163
Total....................	0.1217	0.2168	0.1265	0.1916	0.3225		4.8293

TABLE 6.—*Influence of Grain-size and Hardness of Test Pieces Upon Rate of Corrosion, Expressed as Grams Lost Per Square Inch of Surface Exposed*

Anneal	750° C.	650° C.	550° C.	450° C.	Totals
Copper					
Annealed	0.0136	0.0156	0.0105	0.0122	0.0519
1 number hard.	0 0104	0 0107	0.0110	0.0112	0.0433
2 numbers hard	0.0095	0 0086	0.0101	0 0106	0.0388*
4 numbers hard	0.0148	0 0144	0.0112	0 0116	0.0520
6 numbers hard.	0.0152	0.0129	0.0116	0.0087	0.0484
Total	0.0635	0 0622	0 0544	0 0543*	0 2344
Gilding and Commercial Bronze—97 per cent. to and including 85 per cent. copper					
Annealed	0 0245	0 0206	0 0239	0 0221	0.0911
1 number hard	0 0243	0 0195	0.0259	0 0260	0 0957
2 numbers hard	0.0223	0.0177	0 0232	0.0228	0.0860*
4 numbers hard.	0.0234	0 0255	0 0251	0 0302	0.1042
6 numbers hard	0.0238	0 0278	0.0288	0.0236	0.1040
Total	0.1183	0.1111*	0 1269	0.1247	0 4810
Low Brasses—85 per cent. to and including 70 per cent. copper					
Annealed	0 0114	0.0110	0.0110	0.0114	0 0448
1 number hard	0.0102	0 0104	0.0103	0.0118	0.0427*
2 numbers hard	0.0112	0.0102	0.0118	0 0118	0.0450
4 numbers hard	0 0120	0.0127	0.0108	0.0123	0 0478
6 numbers hard	0 0125	0.0111	0.0116	0.0112	0 0464
Total	0 0573	0 0554*	0 0555	0 0585	0.2267
Brasses—70 per cent. to and including 65 per cent. copper					
Annealed	0.0185	0.0208	0.0201	0.0186	0.0780
1 number hard.	0.0185	0.0182	0.0172	0 0157	0.0696
2 numbers hard	0.0194	0.0181	0 0160	0 0164	0.0699
4 numbers hard	0.0162	0.0172	0 0165	0.0178	0.0677*
6 numbers hard	0.0175	0.0177	0.0182	0.0169	0.0703
Total	0 0901	0 0920	0 0880	0.0854*	0.3555
Muntz Metals—63 per cent. to and including 60 per cent. copper					
Annealed	0.0285	0.0359	0.0372	0.0342	0.1358
1 number hard.	0.0269	0.0306	0.0326	0.0338	0.1239*
2 numbers hard	0.0304	0.0310	0.0333	0.0368	0.1315
4 numbers hard	0.0287	0.0340	0.0323	0.0354	0.1304
6 numbers hard	0.0311	0.0301	0.0375	0.0323	0.1310
Total	0.1456*	0.1616	0.1729	0.1725	0.6526

*Indicates the points of least loss in weight.

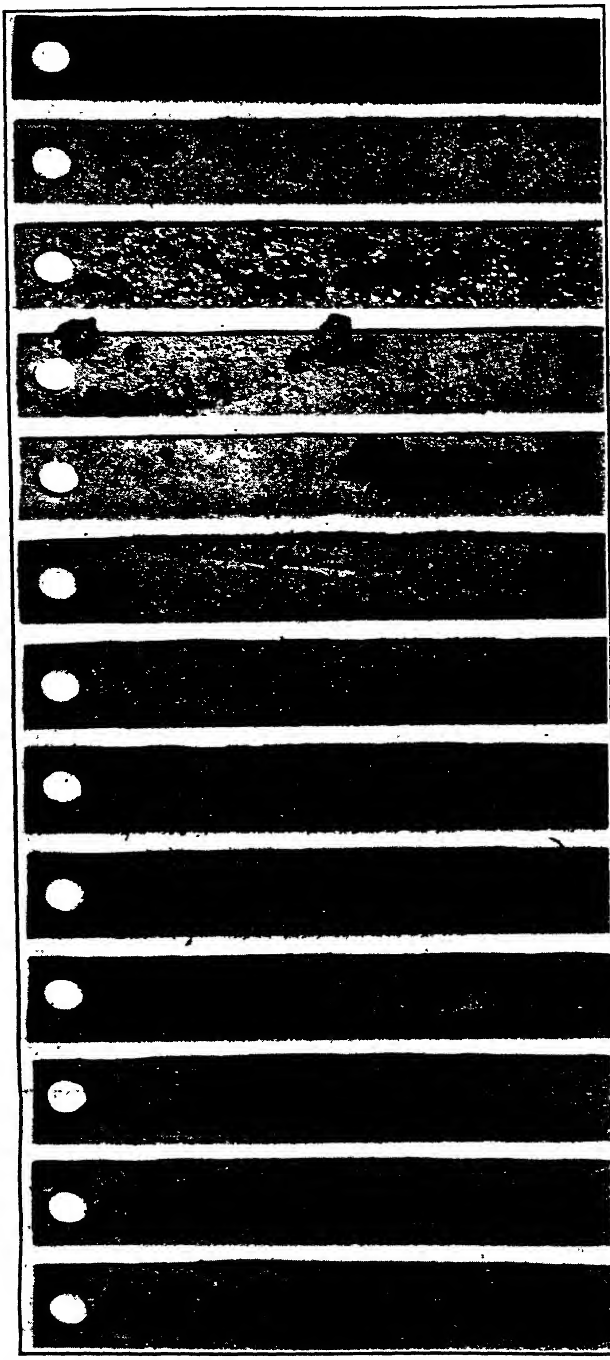
TABLE 6.—*Continued*

Anneal	750° C.	650° C.	550° C.	450° C.	Totals
Bronzes—Copper-tin alloys					
Annealed	0 0197	0.0184	0.0210	0.0194	0.0785
1 number hard	0.0152	0.0155	0.0152	0.0173	0.0632
2 numbers hard	0 0141	0.0143	0.0128	0.0140	0.0552*
4 numbers hard	0.0132	0.0139	0.0140	0.0153	0.0564
6 numbers hard	0.0117	0.0135	0.0165	0.0138	0.0555
Total	0 0739*	0 0756	0 0795	0.0798	0.3088
Copper-zinc-tin alloys					
Annealed	0.0339	0.0377	0.0400	0.0301	0.1417
1 number hard	0 0278	0.0283	0 0276	0 0302	0 1139*
2 numbers hard	0 0293	0 0253	0.0320	0.0321	0.1187
4 numbers hard	0 0337	0.0276	0 0295	0.0314	0.1222
6 numbers hard	0 0316	0 0293	0.0351	0 0322	0 1282
Total	0.1563	0.1482*	0.1642	0.1560	0.6247
Copper-nickel alloys					
Annealed	0 0436	0.0428	0 0467	0.0440	0.1771
1 number hard	0 0386	0 0394	0 0398	0 0383	0 1561
2 numbers hard	0 0395	0 0399	0.0379	0 0382	0.1555
4 numbers hard	0.0379	0 0406	0.0383	0.0398	0.1566
6 numbers hard	0 0375	0.0380	0.0362	0.0378	0.1495*
Total	0.1971*	0.2007	0.1989	0.1981	0.7948
Aluminum bronzes					
Annealed	0 0238	0.0241	0.0223	0.0229	0.0931
1 number hard	0.0215	0.0205	0.0204	0 0223	0.0847
2 numbers hard	0.0243	0.0250	0.0189	0 0191	0.0873
4 numbers hard	0.0214	0.0235	0.0202	0.0182	0 0833
6 numbers hard	0.0210	0.0219	0.0161	0.0175	0.0765*
Total	0.1120	0.1150	0.0979*	0.1000	0.4249

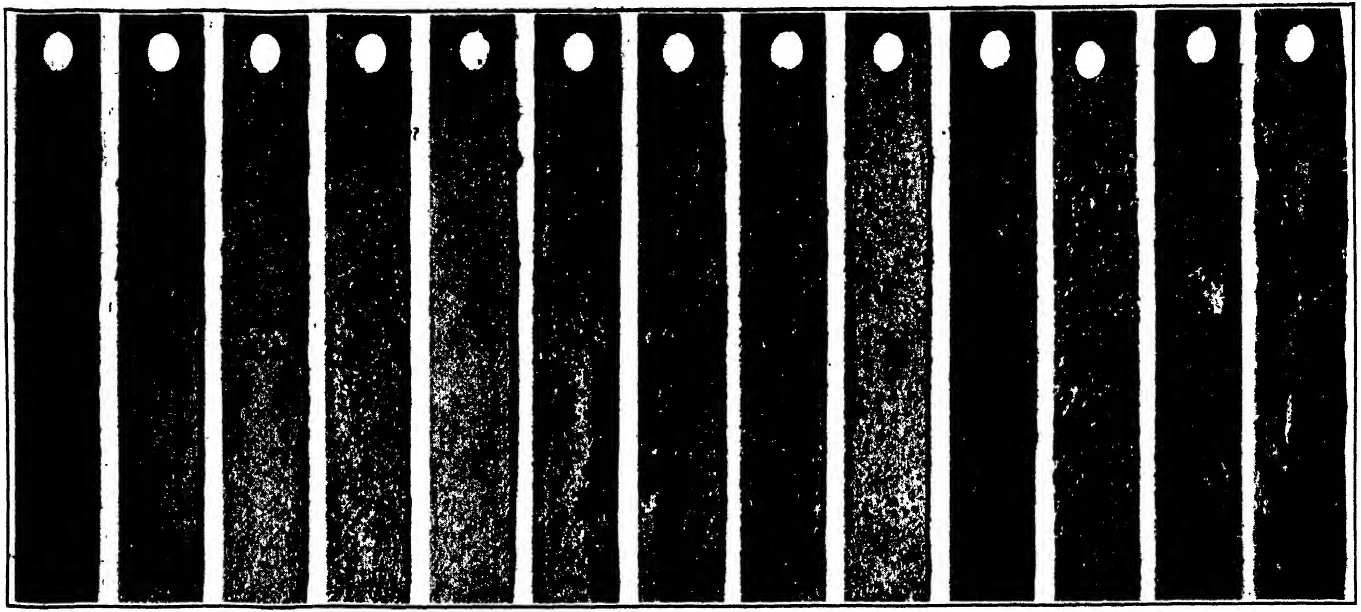
* Indicates the points of least loss in weight.

Periodical Examination of Corroded Metal

During the first year, the specimens were removed every two months and scoured with a stiff bristle brush to remove all loose scale and salts formed by corrosion. After cleaning in this manner, the pieces were weighed with an accuracy of 0.01 gm. The individual samples weighed from 16 to 40 gm. each. All the data for each specimen have been


Per Cent.
Copper 99.94 | 97 | 95 | 90 | 80 | 72 | 66⅔ | 65 | 63 | 61½ | 60 | 66¼ | 95
Zinc........ | 3 | 5 | 10 | 20 | 28 | 33⅓ | 35 | 37 | 38½ | 40 | 33¼ Pb ½ | 5 Sn

(a)

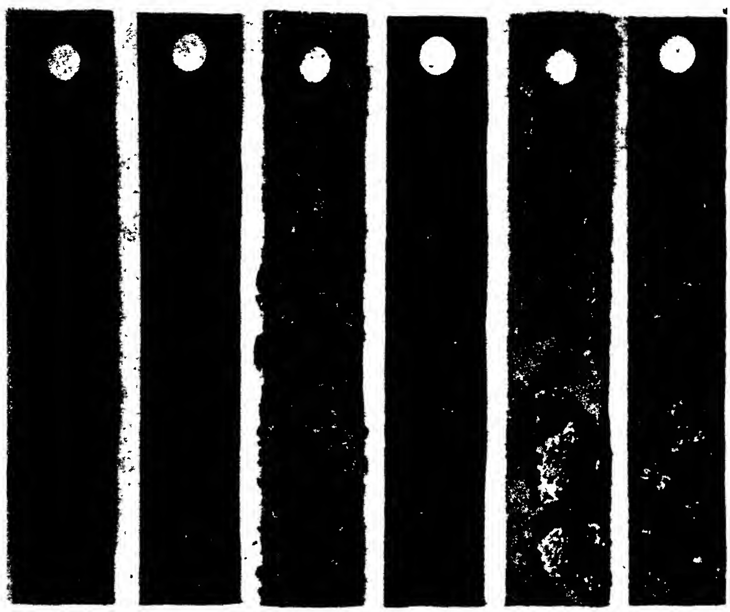


Per Cent.													
Copper	92	93	81	70	60	75	80	85	56⅔	90	95	95½	92
Zinc		6½	18	29	39¼				28⅓			Sn 4	
Tin	8	½	1	1	¾	Ni 25	Ni 20	Ni 15	Ni 15	Ni 10	Al 5	P ½	Al 8

(*b*)

FIG. 3.—AT END OF 18 MONTHS, CORROSION PRODUCTS WERE QUITE DISTINCTIVE; PHOTOGRAPH OF ONE COMPLETE SET OF SPECIMENS REVEALS CHARACTERISTICS THAT ARE SHOWN AT HIGHER MAGNIFICATIONS IN FIGS. 5 AND 6.

assembled into totals arranged according to alloys, also according to hardness or temper, and anneals; these are to be found in Tables 4, 5, and 6 and are graphically shown in Fig. 8. It was soon evident that, so far as corrosion and loss of weight were concerned, conclusions applied almost equally to all (21) specimens of a single alloy irrespective of temper. After the first year, the specimens were cleaned and inspected every six months but were weighed only after longer intervals. Photographs and photomicrographs of the corroded surfaces completed the inspection.

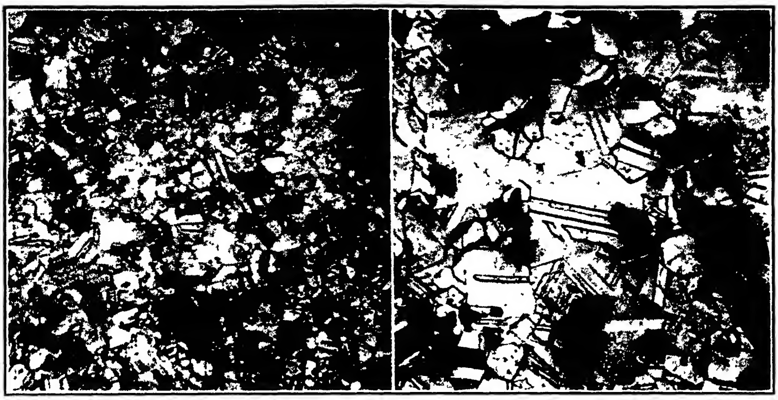


Per cent.						
Copper	60	60	95	95	92	92
Zinc	40	40				
Aluminum			5	5	8	8

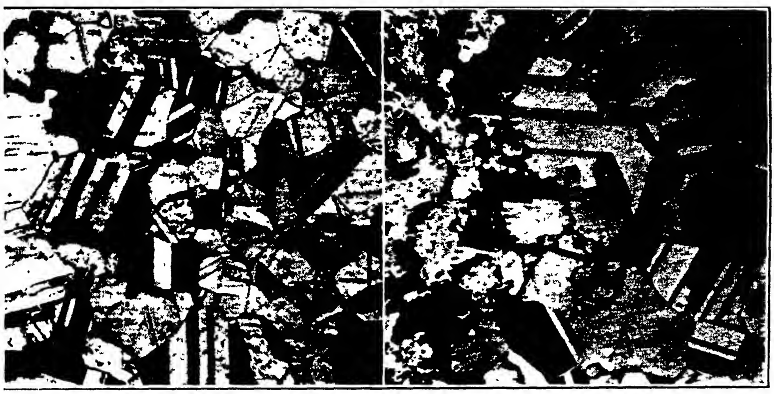
FIG. 4.—MUNTZ METAL AND ALUMINUM BRONZE SHOWING DEZINKIFICATION AND PITTING, RESPECTIVELY, AT END OF 18 MONTHS; ALTERNATE SPECIMENS HAVE HAD PRODUCTS OF CORROSION REMOVED.

Copper-zinc Alloys

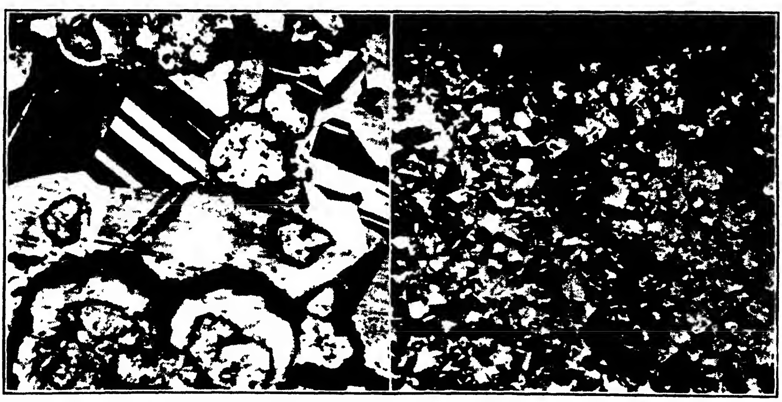
From the first, it was found that of the copper-zinc alloys those ranging from 70 to 85 per cent. resisted corrosion better than the others. The Muntz metal lost little in weight at the beginning but, as dezinkification progressed and the loose friable salts crumbled, the losses progressed rapidly. Pure copper and copper with small amounts of zinc, up to 10 per cent., also had heavy losses from the start. The point of lowest loss is in the neighborhood of 80 per cent. copper. A plot of the losses of the copper-zinc series during each period is given in Fig. 9.



Copper | Copper 95 per cent., zinc 5 per cent.

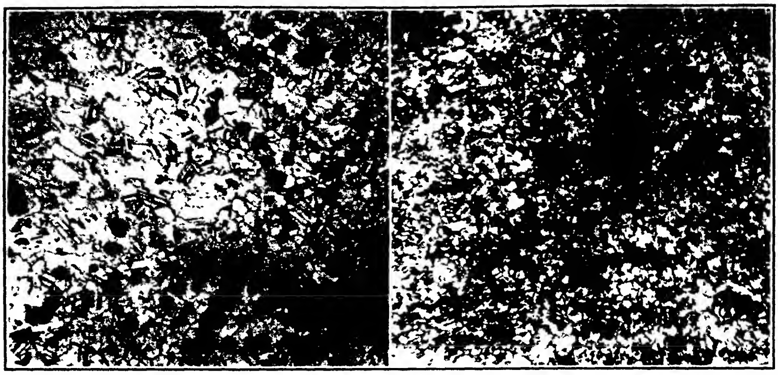


Copper 80 per cent., zinc 20 per cent. | Copper 70 per cent., zinc 30 per cent.



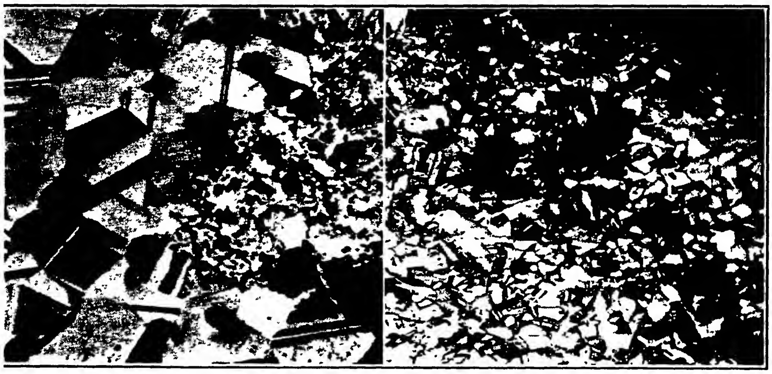
Copper 65 per cent., zinc 35 per cent. | Copper 60 per cent., zinc 40 per cent.

FIG. 5.—TYPES OF CORROSION OF COPPER-ZINC SERIES; RAGGED-EDGED AREAS IN 70 PER CENT. COPPER ALLOY AND BELOW ARE DEZINKIFIED. × 75.



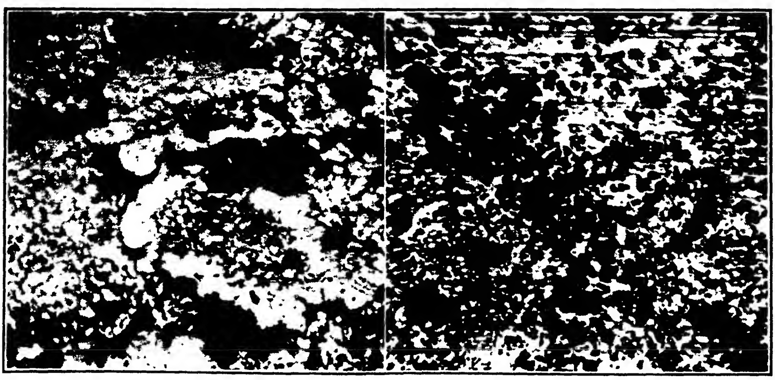
Bronze
Copper 92 per cent., tin 8 per cent.

Copper 75 per cent., nickel 25 per cent.



Admiralty alloy
Copper 70 per cent., zinc 29 per cent., tin 1 per cent.

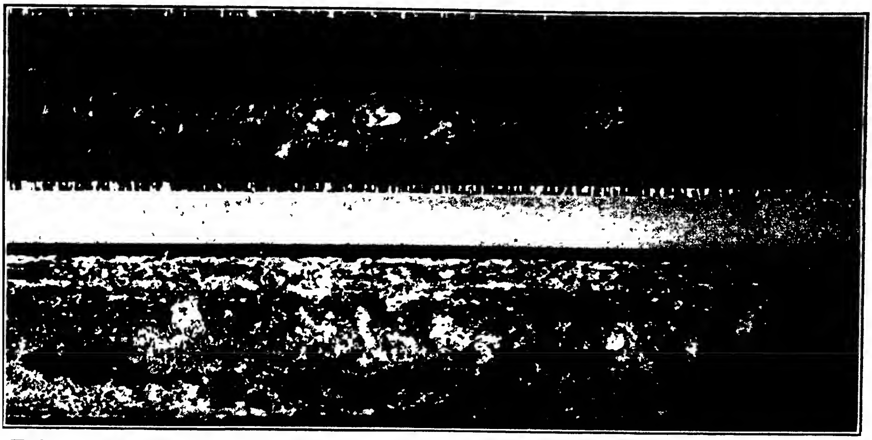
Aluminum bronze
Copper 92 per cent., aluminum [illegible] per cent.



Manganese bronze
Copper 59 per cent., zinc 39 per cent., tin, 0.70 per cent., iron 0.80 per cent., manganese 0.50 per cent.

Tobin bronze
Copper 60 per cent., zinc 39.25 per cent., tin 0.75 per cent.

FIG. 6.—TYPES OF CORROSION, EVEN SOLUTION OF BRONZE AND CUPRO-NICKEL, DEZINKIFICATION OF MANGANESE AND TOBIN BRONZE, PITTING OF ALUMINUM BRONZE. × 75.



Tube, copper 95 per cent., zinc 5 per cent.; failed by pitting in 2 years, 11 months.

Tube, copper 70 per cent., zinc 30 per cent. (tinned upon inner surface); failed by pitting in 2 years, 11 months.

Tube, copper 92 per cent., aluminum 8 per cent.; failed by pitting in 3 years, 7 months.

Copper-nickel Alloys

Copper alloys containing from 10 to 25 per cent. nickel suffered approximately equal losses in weight from corrosion; see Fig. 10. These losses were greater than in the case of the best of the brasses. The nickel alloy of 57 per cent. of copper, 28 per cent. of zinc, and 15 per cent. of nickel lost much less than the cupro-nickels. It compared favorably with the brasses containing about 70 per cent. of copper in tenacity of scale and loss in weight.

A characteristic of the nickel alloys is the flaking off of the scale formed by corrosion, if allowed to become dry, and the consequent loss of pro-

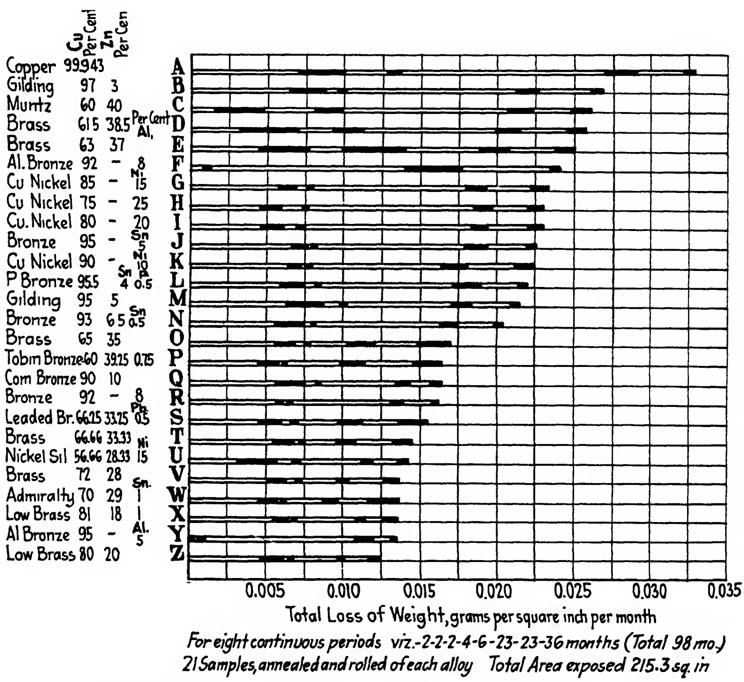


FIG. 8.—CORROSION OF COPPER ALLOYS IN SEA WATER.

tection usually afforded in this manner to some of the alloys. Under actual service conditions, therefore, the nickel alloys described might make a poorer showing than these experimental tests would indicate.

Copper-tin Alloys

Increase in the tin content of bronzes aids resistance to corrosion. Those with 5 per cent. of tin, including the phosphor-bronze, suffer greater loss than those having 8 per cent. tin. In general, it would appear that the bronzes, copper-tin only, lose less than the cupro-nickel alloys but more than the high-copper brasses.

Copper-aluminum Bronzes

The aluminum bronzes kept their original smooth surface finish without tarnishing or corroding and lost practically nothing in weight for several months; then small round pits appeared around the edges of the samples and along scratches. These pits continued to grow in size and depth slowly during the first year (see alloys *F* and *Y*, Fig. 8) but rapidly thereafter. The aluminum bronzes, which for a year showed hardly any corrosion, at the end of 18 months were badly pitted, some of the pits passing completely through the specimen. The scale covering the samples was deep green, with large patches of white aluminum salts covering the pitted areas. Near the pits were deposited

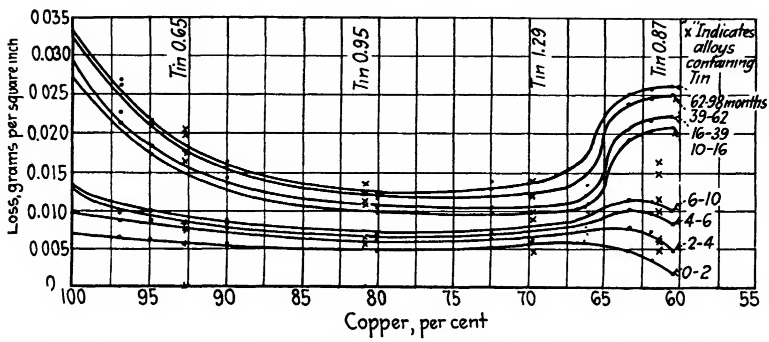


FIG. 9.—COMPARISON OF RATES OF LOSS OF BRASSES BY CORROSION IN SEA WATER; TOTAL TIME, 98 Months; TOTAL AREA EXPOSED, 215.3 SQ. IN. OF EACH ALLOY; 21 SAMPLES ANNEALED AND ROLLED OF EACH ALLOY.

thin areas of reddish-purple copper; this deposit was hard and firm and gave the only positive evidence of redeposition on the surface of the samples. Fig. 4 shows the aluminum bronzes with scale and with scale removed; it illustrates the wide pitted areas and adjacent copper deposits. White incrustations of aluminum salts build up over each pit in large spongy masses. For comparison Muntz metal specimens are shown in the same photograph.

In the plotted results (Fig. 8), the 5 per cent. aluminum bronze occupies a very favorable position next to low brass. But considering the depth of pitting characteristic of all the specimens the aluminum bronzes are not worthy of the position and from our present knowledge must be judged inferior to several of the other alloys investigated. The fact remains, however, that after 98 months immersion in sea water portions of the original surface are still intact.

Copper-zinc-tin Alloys

Alloys of copper, zinc, and tin form a corrosion-loss curve similar to that of brass (Fig. 9). Where the beta constituent is present, how-

ever, as in Tobin bronze, the tin undoubtedly increases the resistance of the alloy to sea-water corrosion, the losses being similar to those of the brasses rather than to those of Muntz metal. Experience with Tobin bronze in actual service bears out the truth of these conclusions.

Lead

A small amount of lead (0.50 per cent.) in brass appears to have no appreciable effect on the rate or manner of corrosion by sea water.

Effect of Annealing or Grain Size on Corrosion

In Tables 4, 5, and 6 are given, in detail, the total losses of the specimens grouped in such a manner that one may verify the conclusions which follow:

Influence of Hardness and Grain-size of Test Pieces upon Rate of Corrosion

When considered as groups, the alloys suffered least loss when hard rolled to the extent here given:

	Annealed at Degrees C.	Finished with Reduction, Per Cent.
Copper	450	20.7
Gilding and commercial bronze	650	20.7
Low brasses	650	10.9
Brasses	450	37.1
Muntz metals	750	10 9
Bronzes	750	50.0
Bronzes	650	10.9
Cupro-nickels	750	50.0
Aluminum bronzes	550	50.0

Annealed specimens lost more than the hard-rolled material, but the annealing temperatures at which least loss occurred are as follows:

	Annealed at Degrees C.		Annealed at Degrees C.
Copper	550	Bronzes (Cu-Sn)	650
Gilding and commercial bronzes	650	Bronzes (Cu-Zn-Sn)	450
Low brasses	550–650	Cupro-nickels	650
Brasses	750	Aluminum bronzes	550
Muntz metals	750		

Accelerated Corrosion by Salt Spray

Description of Apparatus

The apparatus used was similar to that used for testing zinc coatings on galvanized articles and described by Finn.[1] It is an inclined Alberene stone box covered with a glass plate and fitted with a spray nozzle operated by compressed air, the samples being supported by a glass rod. The solution used contained 20 per cent., by weight, of common salt (NaCl).

[1] A. N. Finn: *Proc.* A. S. T. M. (1918) **18**, 237.

At the approximate time of the completion of the 10-year sea-water tests, a 1-year test by salt spray was undertaken on a copper-zinc series from pure copper down to 60 per cent. copper and 40 per cent. zinc. Commercial copper and twelve alloys in sheet form 4 by 4 by 0.020 in. gage, and annealed, were suspended on glass rods and subjected to the regular 20 per cent. salt spray.

The loss in weight results are expressed graphically in Fig. 11. The curves are characteristically the same as those shown for losses by weight of similar alloys in sea water, Fig. 9. As in the case of those in sea water, the alloys from copper to 85 per cent. copper and 15 per cent. zinc pitted, and those from 75 per cent. copper to 60 per cent. copper dezinkified. The actual depth of pits was from 6 to 12 times the depth of calculated average penetration by solution, and the depth of dezinkification, though not measured, was apparently as great or greater than the depth of the pits in the samples that were not dezinkified. Depth of either pitting or dezinkification actually determines the life of the alloys in the copper-zinc series.

The salt-spray test affords a convenient and satisfactory means for the study of the rates of corrosion for continuous periods of different lengths. It is also indicative of the true relative resistance of the alloys, whereas in the sea-water tests the initial rates of loss were very low, for instance in the case of Muntz metal, and consequently were misleading.

From a practical standpoint the salt-spray and sea-water tests both show that the better alloys are not endangered but are rather protected by the presence of corrosion scale, whereas the alloys having a tendency to become pitted and dezinkified are progressively, and perhaps more violently, attacked beneath the scale.

A minimum test in salt spray of 3 months duration seems essential for the alloys under discussion.

Conclusions

Tubes of many alloys successfully withstood the 10-year attack of the sea water by solution, pitting, or dezinkification. In order to select or to predict those that would be the best, it will be necessary to rely on visual and microscopic examination (where the personal element is introduced) as well as on the loss in weight data supplied by sea-water and salt-spray tests on small sheet-metal specimens of similar composition. It is apparent that a selection of material best suited to resist salt-water corrosion should avoid the tendency toward both pitting and dezinkification. The copper-zinc series should be homogeneous alpha brass of the region between 70 and 85 per cent. copper. If tin can be added to these alloys, so as to become a part of the solid solution, no apparent harm is done. In fact, previous investigations as well as practical service conditions have tended to show that in many cases the addition of tin to alloys for use

with salt water was beneficial. For instance, in this experiment, the length of life of a Muntz (60 per cent. copper and 40 per cent. zinc) type of tube was increased from 2 to more than 10 years by the addition of tin (Tobin bronze).

Tinning or tin-plating in a commercial manner the inner surface of the tubes appears to retard the corrosion of Muntz metal for a month or two but, in the case of 70–30 copper-zinc alloys, the presence of tin on the surface has caused severe dezinkification and failure. Furthermore, tinned Admiralty tubes in harbor and sea-water service, in several instances brought to our attention, failed by dezinkification and deep pitting. Rather than tinning the condenser tubes, it would be considered better practice to choose the alloy best fitted to withstand the service conditions.

Of the other alloys, those that appear to be serviceable include the copper-tin mixtures of the alpha region and the cupro-nickels and copper-nickel-zinc alloys. The bronzes (Cu-Sn) do not become pitted but dissolve slightly and evenly, the losses in weight being somewhat greater than those of the better brasses. The bronzes and nickel alloys rank together in this respect, both the sheet and tube samples being in good condition at the end of the test.

Of the nickel alloys, the copper-nickel-zinc specimens formed a firmer corrosion scale, which was protective and did not easily flake off—that upon the cupro-nickel (Cu-Ni) came off easily, especially on drying, which fact apparently explains the greater loss in weight of those specimens. The nickel alloys dissolved evenly and did not become pitted but they appear less suitable for condenser tubes than the best of the brasses. They lose more in weight, cost more, and are more difficult to manufacture; hence are more liable to faults than the brasses of the 70 to 80 per cent. copper region. These last considerations likewise apply to the bronzes (copper-tin).

The alloys unsuitable for condenser tubes would include the brasses above 85 per cent. copper, those below 70 per cent. copper, manganese bronze, and aluminum bronzes. Pitting or dezinkification causes tubes of these alloys to fail rapidly.

The brasses best fitted by composition for use with sea water resist corrosion to the fullest extent when finished with a 10 per cent. reduction following a 650° C. anneal (½ hr. annealing period). Considering annealed specimens only, the brasses were at their best with a 550° to 650° C. anneal, whereas the brasses containing tin, including the Admiralty alloy, were most resistant at the 450° C. anneal. Apparently a slight reduction (10 per cent.) gave the metal a more perfect surface and, consequently, slightly better corrosion resistance, than that which resulted from annealing. This point was noticed especially in the behavior of the sheet specimens during the first year; it was also found that the loss

was greater with the higher anneals than with those at a lower temperature. It should be noted that the annealing of Muntz metal usually produces a surface layer of alpha crystals, which have the practical value of resisting corrosion during the first month or two; after that time, however, the beta grains are reached and action progresses rapidly.

ILLUSTRATIONS

Attention has been called to the illustrations of the apparatus and the condition of the specimens. Fig. 3 shows one set of the sheet specimens with characteristic corrosion scale; generally speaking, the smoother the appearance of the specimen the better its condition. Pits and dezincified areas are hidden beneath mounds of scale. In Fig. 4, however, the scale has been removed from alternate specimens to reveal the dezincification of the Muntz metal and the deep wide pits in aluminum bronze.

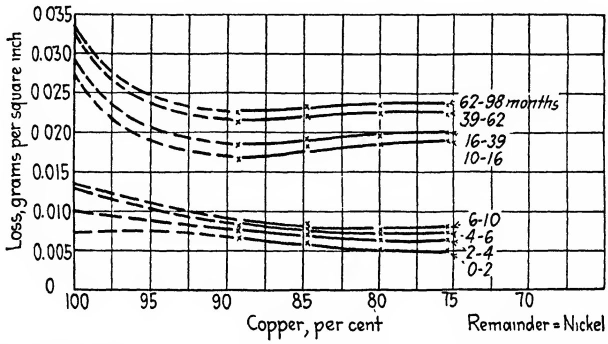


FIG. 10.—COMPARISON OF RATES OF LOSS OF CUPRO-NICKELS BY CORROSION IN SEA WATER; TOTAL TIME, 98 MONTHS; TOTAL AREA EXPOSED, 215.3 SQ. IN. OF EACH ALLOY; 21 SAMPLES ANNEALED AND ROLLED OF EACH ALLOY.

The nature of the attack upon the alloys, as revealed by the microscope, is shown in Figs. 5 and 6. The ragged-edged structureless areas reveal dezincification in common brass, and Muntz and Admiralty alloys. The richer copper brasses are rather deeply pitted, whereas those of about 80 per cent. copper, as well as the nickel alloys, and copper-tin bronzes, are but slightly pitted or dissolved.

In Fig. 7, three characteristic failures of tubes are shown, aluminum bronze, 95 per cent. copper-5 per cent. zinc, and 70 per cent. copper-30 per cent. zinc having the inner surface tinned. In the upper part of the tube, in each case, the corrosion scale has been removed.

Figs. 8 to 10 have been developed from the data in Table 4. All values are expressed as total loss of weight in grams per square inch per month. The apparently great losses during the fifth period were due to more thorough cleaning of all specimens with a blunt instrument to remove all loose scale. Fig. 9 shows the point of least losses for brasses,

and similar alloys containing some tin (marked x). It should be remembered, however, that the alloys below 72 per cent. copper or thereabouts were dezinkified. Fig. 9 should be compared with Fig. 11, which shows losses of similar alloys in the salt-spray test. Here, also, the point of

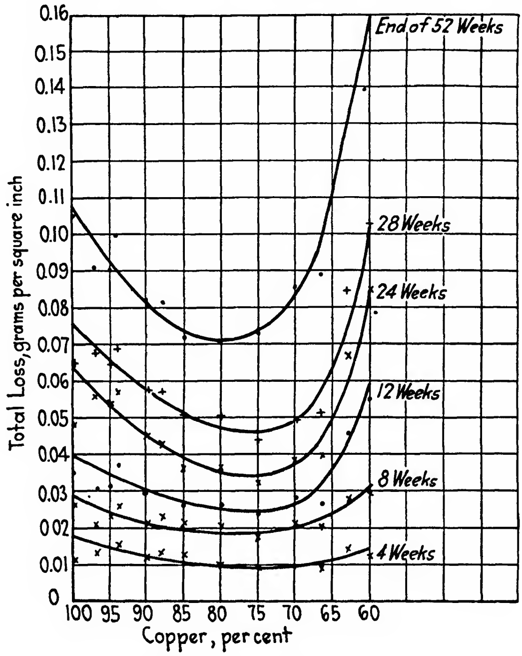


FIG. 11.—SALT-SPRAY CORROSION TESTS UPON COPPER-ZINC ALLOYS; TOTAL LOSSES IN WEIGHT AT END OF PERIODS UP TO 1 YEAR. COMPARE WITH SEA-WATER LOSSES, FIG. 9.

least loss is at 80 per cent. copper and 20 per cent. zinc. The specimens containing 75 per cent. copper were slightly dezinkified. All results, therefore, appear to be in agreement as to the superiority among the brasses of those in the 80 per cent. copper and 20 per cent. zinc region, at least so far as salt-spray and salt-water tests are concerned.

DISCUSSION

W. B. PRICE,* Waterbury, Conn. (written discussion).—The authors are to be congratulated on the unique features of this investigation; *viz.*, length of time of tests, the remarkable agreement of the 10-year sea-water tests and the accelerated salt-spray test.

While the two phases of the investigation were the attack of the sea water upon the walls of the tubes and the rate of solution of weighed

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samples in the same sea water, this investigation does not take into consideration the important effects of corrosion caused by variable speeds of the condenser water with its attendant lodgment of air particles. Another important point, which should be taken into consideration, is the lodgment of foreign deposits of variable nature, such as wood, coke and coal, cinders, slag, etc., which form concentration cells, causing rapid corrosion with resulting pits, generally known as pinhole or regional pitting. Such conditions are also responsible for the plug type of dezincification. In calling attention to these facts, I do so with a realization that it was impossible for the authors to introduce all these variables.

The fact that the water became clear after two or three days and continually passed through the tubes for several months in this condition makes the water in direct contrast to the circulating water encountered in our harbors today, which contains a great deal of dangerous foreign matter. The statement is often made that modern condenser tubes do not last as long as those manufactured some few years ago. The people making these statements do not take into consideration the increased demands upon public-service corporations, which call for different operating conditions such as changes in temperature, pressure, and water speeds. Neither do they take into consideration the fact that many of our harbors are cesspools for adjacent city sewage and waste systems from chemical plants. Condenser tubes produced today by up-to-date manufacturers are practically mechanically and physically perfect. This condition has been brought about by chemical and metallurgical control, and the formulation of standard specifications. The increased demands made upon public-service corporations call for a closer coöperation between the engineers and operating heads of these plants, and the technical departments of the condenser-tube manufacturers than has existed in the past.

On page 770, it is stated that the hard-rolled specimens show less loss by corrosion than the annealed specimens. This conclusion is contrary to the opinion heretofore held, that an annealed tube, especially a fine-grained one, resisted corrosion better than one that was hard-worked. While the authors' tests on the sheet-metal specimens indicate that 80 per cent. copper-20 per cent. zinc combination shows superior resistance to corrosion, at least so far as salt-spray and salt-water tests are concerned, in the case of tubes this superiority does not seem to be so marked; for instance: Admiralty metal annealed (page 753) gives exactly the same life and characteristics under column "Nature of Corrosion" as the low-brass hard tube on page 750. Also, 70-30 brass annealed (page 751), shows no dezinkification and it is stated that the tubes were in fine condition, while the same alloy when drawn hard (page 754) is dezincified. This would seem to indicate that the hard-drawn surfaces might have been responsible for the dezincification.

The writer heartily concurs in the conclusions (page 772) that it is not advisable to tin condenser tubes. It has been our practice never to recommend tinned condenser tubes. These conclusions should go a long way toward discouraging the use of tinned tubes. The statement, on the same page, that the Admiralty alloy was most resistant at the 450° C. anneal agrees with the writer's views regarding the superiority of a fine-grained Admiralty tube.

The authors should supplement their experiments by a practical test in a condenser where local conditions are known to be extremely severe, using for such tests tubes of fine-grained admiralty metal having a grain size not in excess of 0.02 mm, also admiralty metal finished with a 10 per cent. reduction following a 650° C. (½-hr. annealing period), and tubes of 80-20 low brass having a grain size not in excess of 0.02 mm and 80-20 low brass finished with a 10 per cent. reduction following a 650° C. (½-hr. annealing period). Such a test should go a long way toward proving whether the hard-drawn and annealed 80-20 low brass is superior to Admiralty mixture in actual service.

W. R. Webster,* Bridgeport, Conn. (written discussion).—This paper is a welcome contribution to our knowledge of a subject whereon opinions are many and tenaciously held and quantitative supporting data few. Inasmuch as the conditions of exposure differed somewhat from those normally encountered in condenser practice, objection might be raised if too broad conclusions are drawn. On the other hand, they represent by far the most comprehensive data as to the relative resistance of copper and its various alloys to the specific corrosive action of sea water yet recorded.

Some of the conclusions drawn seem scarcely justified, however. It is stated that

> Brasses best fitted by composition for use with sea water resist corrosion to the fullest extent when finished with a 10 per cent. reduction following at 650° C. anneal (½-hr. annealing period). Considering annealed specimens only, the brasses were at their best with a 500° to 650° C. anneal, whereas the brasses containing tin, including the Admiralty alloy, were most resistant at the 450° C. anneal. Apparently a slight reduction (10 per cent.) gave the metal a more perfect surface and, consequently, slightly better corrosion resistance, than that which resulted from annealing.

In Table 5, alloy 81 per cent. copper, 18 per cent., zinc, 1 per cent. tin, 8 numbers hard sample suffered a loss of 0.0052 gm. per sq. in. surface exposed. The five samples annealed at 750° C. and drawn to various tempers showed an average loss of 0.0054; the succeeding group annealed at 650° C., an average loss of 0.0051; the group annealed at 550° C., an average of 0.0053 and the group at 450° C., an average loss of 0.0053; while the grand average for anneals and tempers was 0.0053. Using the 8 numbers hard sample as a control, it would appear that the various

* Vice-president Bridgeport Brass Co.

tempers and anneals involved were without effect. The corresponding figures for alloy 70-29-1 are 0.008 for the 8 numbers hard; 0.0079; 0.0071; 0.0088; 0.0082 and 0.0080.

The supposedly beneficial effect of tin in condenser tubes is not borne out. The 80-20 mixture without tin gives a total loss for the entire series of 0.1068, whereas the same mixture with 1 per cent. tin gives 0.1108. The 72-28 samples gave a total loss of 0.1340 as against 0.1676 for the 70-29-1.

It is interesting to note that the presence of 0.5 per cent. of lead produced no abnormal corrosion. This is important in view of the customary practice of regarding tubes containing as much as 0.1 per cent. of this element as dangerously contaminated.

George A. Orrok, New York, N. Y.—The tests described were made with water taken from the East River at 42d St., very close to the Waterside Station. Most of the troubles with our condenser tubes at Waterside, I believe, are caused by the presence in the sea water of nitrates and ammonia compounds, which affect brass tubes in a rather serious manner. Also, the heating up, during the passage through the condenser, of this water with its gaseous chemical compounds has a great deal to do with the corrosive action. This part of the action was practically eliminated in the tests described because the water was circulated over and over again, and after a very short time what I call the active part of the sewage in the water was dissipated in the air.

A. E. White,* Ann Arbor, Mich.—We run across some curious instances in studying condenser-tube failures. For instance, the aluminum-bronze shown here has an excellent life but in one plant the life of aluminum-bronze tubes has been exceedingly disappointing. In some plants, monel-metal tubes have a greater life than the Admiralty tubes. Yet an Admiralty condenser tube, at least for sea water, is superior to an ordinary monel-metal condenser tube. The chart on page 768 might cause us to believe that the 72-28 brass would give as good results as an Admiralty tube, yet operating engineers prefer an Admiralty tube for sea water.

The life of condenser tubes, within the past few years, has been greatly increased. We must look at the situation from a two-fold viewpoint: (1) What effect has the method of operating a condenser on its tube life? (2) will it be possible for us to get a master alloy that will give us a life of 15 to 25 years?

Our experiments with non-ferrous alloys, in increasing the life of different brasses and bronzes, indicate that one type may be superior to another, but they are only differences in degree. They do not solve

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the problem, and we should direct some of our research work toward finding a master alloy that will give us increased life over that now obtainable from any of the alloys used for condenser-tube manufacture.

Probably some of the conditions in condenser operation that we ought to know about are the nature of the packing, the temperature of the water at both the inlet and the outlet end of the condenser tube (because one tube may be operating under such conditions that its temperature is much higher than it is in other tubes), the character, velocity, and the quantity of the water, the velocity and quantity of the steam, the distance between supports, and especially the manner in which the water enters the condenser. It is common condenser experience that most tubes fail a given distance from the head end of the condenser; therefore, not only must our investigations be carried on with regard to our present alloys but also with regard to the condenser operation.

D. K. Crampton,* Waterbury, Conn. (written discussion).—This paper shows the result of a long and very instructive investigation on a subject that heretofore has not received even a small part of the attention it deserves. The results of this work should go a long way toward showing what factors are of importance in salt-water corrosion. Users of condenser tubes, in particular, should derive much benefit by a careful study of this paper. In particular, the findings in the matter of grain size, temper, tin and lead content, and tin coating admit of direct practical application. In the past, specifications for condenser tubes have been drawn up on a purely empirical basis and without regard to the real needs of the occasion. Such work as this should tend to bring about a much needed change in this field.

In spite of the general excellence and usefulness of the paper, it seems desirable to call attention to a few apparent shortcomings.

In Table 1 are given the analyses of a few lots of water used in the experiment. There is considerable difference in the analyses of the different lots of water and the analyses of new and old water of any one lot are not quoted. It is, therefore, impossible to tell, at least from the published figures, what the effect of six months' test had on the analysis of the water itself. The question naturally arises as to the effect of the differences in analysis on the corrosion during any one period. It is quite possible that the complete data would throw some light on the variations in rate of attack during the different periods.

The sheet specimens used were scoured every two months with a stiff bristle brush during the first year to remove all loose scale and salts formed by corrosion. Thereafter this same treatment was applied every six months for the duration of the test. In addition, at the end of 16 months, the specimens were somewhat more drastically cleaned with

* Metallurgist, Chase Metal Works.

the aid of a blunt instrument. Quite possibly this periodic cleaning may have had a marked effect on the corrosion in the subsequent periods and a greater effect on certain alloys than others. In this event, the total relative corrosions for the whole period might well not correspond with what would be obtained if the specimens had not been cleaned.

It is stated that brasses containing less than 75 per cent. copper, including Admiralty, usually show dezincification rather than pitting. While in general this is true, brasses as low as 64 per cent. in copper often pit rather than dezincify and, in the case of Admiralty metal, pitting is by far the most prevalent type of attack.

In Fig. 11, giving the results of salt-spray corrosion tests upon various copper-content brasses, for all periods up to and including 28 weeks the minimum corrosion is experienced with approximately 75 per cent. copper. With a 52-week exposure, however, the minimum point shifts to approximately 80 per cent. copper. The question naturally arises as to whether, in a longer period—say, two or more years—this minimum point would remain at 80, swing back toward 75, or possibly approach even nearer the pure copper end.

In Table 4, under the first 8 columns there are listed the losses in weight in grams per square inch per month of the various sheet alloys for different periods of the test. The first three columns are averages of 2 months' exposure, the fourth of 4 months', the fifth of 6 months', the sixth and seventh of 23 months' each, and the eighth column of 36 months'. In the ninth column is given a total figure which is the summation of the individual rates listed in the first eight columns. This so-called total figure is *not* the actual total loss in grams per square inch but is simply an unweighted summation of the rates of attack during unequal periods and has no real physical significance. The figures listed in column 9 have, however, been used in plotting Fig. 8, 9, and 10, so that these figures in turn are incorrect. If the figures for the losses per month were multiplied by the number of months and these products added up for the eight periods, the totals obtained would be the same as the totals listed in Table 5 for the same alloys. As an example, alloy A in Table 4 should contain in the last or total column the figure 0.2495 rather than 0.03309. If these totals should be divided by 21 (the number of samples) the results for each alloy would be the average loss in grams per square inch of surface for the entire 98-month period. These corrected figures have been plotted in the accompanying diagram, Fig. 12, which should be compared with the top curve in Fig. 9 in the original paper. In general, the curve thus obtained shows the same characteristics as those in Fig. 9, and the same conclusions would be reached; *viz.*, that the maximum resistance to corrosion is obtained at approximately 80 per cent. copper. As will be shown, however, it is by no means sure that figures for rate of wall penetration would lead to the same conclusions.

In the third paragraph of the description of the accelerated corrosion by salt spray, on page 771, it is stated "The actual depth of pits was from six to twelve times the depth of calculated average penetration by solution, and the depth of dezincification, though not measured, was apparently as great or greater than the depth of pits in the samples that were not dezincified. Depth of either pitting or dezincification actually determines the life of alloys in the copper-zinc series." This statement would hardly be questioned by any one conversant with the corrosion of copper alloys. In spite of this, however, the authors have neglected entirely to measure, or at least to report, measurements of depth of pitting and dezincification and have based their entire conclusions on loss of weight figures. This is illogical and detracts considerably from the value of the

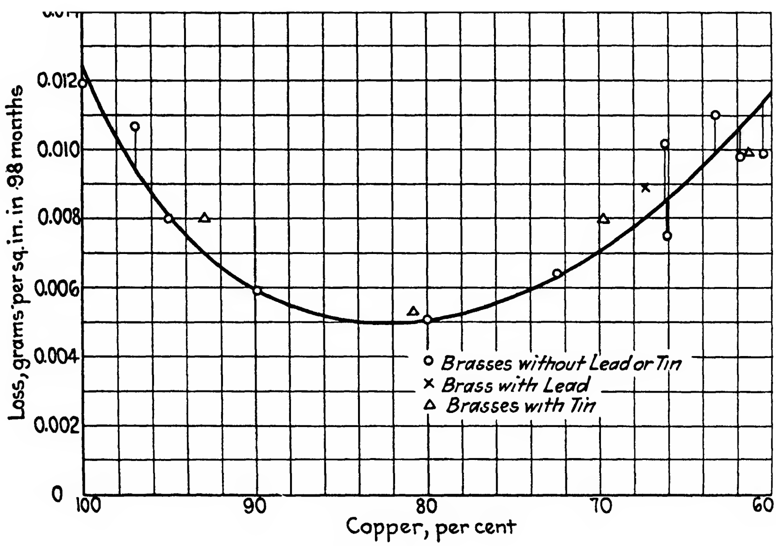

FIG. 12.

experiment. The same remarks hold true in the case of the tubes and sheet metal used in the 10-year salt-water immersion test.

As no figures whatever were presented covering depth of attack either by pitting or dezincification on the sheet samples, there is no way of telling whether such measurements would or would not corroborate the findings based on loss of weight. In the case of the tubes themselves, reported in Table 2, however, there are some interesting facts disclosed indicating that the depth of penetration by pitting or dezincification leads to quite different conclusions than are drawn from loss of weight measurements. In Table 7, are given figures on rate of penetration as computed from data given in Table 2. The figures are accurate only in so far as the remarks under "Nature of Corrosion" in Table 2 give actual accurate measurements.

Table 7 shows many interesting and instructive points not brought out by the loss of weight figures. First, six alloys show less than 0.001-in. penetration per year; these are classed as excellent and include Tobin bronze, Admiralty, 15 per cent. cupro-nickel, 15 per cent. nickel-silver, and leaded high brass, in addition to low brass, which loss of weight experiments indicates as the best. Fourteen others show rates of penetration of from 0.001 to 0.005 in. per year and are classed as fair. Eleven groups show from 0.005 to 0.050 in. penetration per year and are classed as poor. Some or all of the tubes of each alloy of this latter class actually corroded clear through the tube wall in the 10-year period, and often in much shorter times.

TABLE 7.—*Depth of Penetration of Pitting or Dezincification*

(Compare with Table 2 of original paper)

Rating	Alloy	Tube Numbers	Rate of Wall Penetration, Inches per Year	Class
1	Tobin bronze	106–110	0.0003	Excellent
2	Low brass	21– 25	0.0005	Excellent
3	Admiralty	96–100	0.0005	Excellent
4	Cupro-nickel (15 per cent)	126–130	0.0005	Excellent
5	Nickel-silver	131–135	0.0005	Excellent
6	Leaded high brass	76– 80	less than 0.0010	Excellent
7	Copper	1– 5	0.0013	Fair
8	Commercial bronze	11– 15	0.0015	Fair
9	Bronze	81– 85	0.0015	Fair
10	Bronze	91– 95	0.0016	Fair
11	Brass	26– 30	0.0018	Fair
12	Cupro-nickel	121–125	0.0020	Fair
13	Cupro-nickel	136–140	0.0020	Fair
14	Tinned brass	36– 40	0.0025	Fair
15	Brass	51– 55	0.0025	Fair
16	Aluminum bronze	111–115	0.0025	Fair
17	Tinned brass	41– 45	0.0027	Fair
18	Bronze	116–120	0.0033	Fair
19	Brass	56– 60	0.0040	Fair
20	Aluminum bronze	141–145	0.0049	Fair
21	Brass	46– 50	0.017	Poor
22	Rich low brass	16– 20	0.017	Poor
23	Gilding	6– 10	0.020	Poor
24	Aluminum bronze	146–150	0.022	Poor
25	Bronze	88– 90	0.022	Poor
26	Gilding	86– 87	0.029	Poor
27	Tinned muntz	66– 70	0.029	Poor
28	Muntz	71– 75	0.045	Poor
29	Muntz	61– 65	0.045	Poor
30	Muntz	31– 35	0.045	Poor
31	Manganese bronze	101–105	0.045	Poor

Particular attention is called to the four groups of muntz-metal tubes showing 0.029 to 0.045 in. penetration per year. Based on such figures, the rate of attack to muntz metal is on the order of 100 times as great as that of the alloys of class 1 instead of twice as great, as the loss of weight figures would indicate. It should also be noted that the high brass containing lead compares very favorably with low brass, Admiralty, and the other class 1 alloys. The paper states that lead apparently has no appreciable effect on the rate or manner of corrosion by sea water; the depth of pitting measurements, however, would indicate that this amount of lead has a very beneficial effect on high brass. Attention is also called to the fact that both gilding metal and rich low brass (95-5 and 85-15 copper-zinc alloys) make a much poorer showing on a basis of penetration measurements than loss of weight measurements. Finally, 15 per cent. cupro-nickel appears to be decidedly better than either a 10 or 25 per cent. cupro-nickel, judged on the basis of depth or penetration of attack.

It is quite possible that the authors have more complete data on depth of penetration by pitting or dezincification than they published. If so, a supplement to the paper giving such data would be of extreme value. Certainly, in the case of condenser tubes, pipelines, etc. this is an all-important factor, whereas loss of weight over the general area is of relatively little importance.

William H. Bassett (author's reply to discussion).—In carrying out this work in the laboratory, it was impossible to have a continuous flow of fresh sea water and the cleaning of the sea water by aeration was a very interesting phenomenon. This, of course, oxidized organic matter but considerable ammonia remained in all of the samples of water when thrown out for replacement. When we began we hoped to use an elevated temperature, though perhaps not steam temperatures, but on account of the steam from the sea water, and also its action on wooden headers, we had to content ourselves with room temperatures. If we could have carried on the test under actual operating conditions, it would have been more satisfactory. The test was under way and although we could not operate quite as intended we hoped it would show something of the relative values of these alloys, that it would give an indication of their relative value for condenser purposes, and thus give us some idea of which alloys to recommend for test under future operating conditions.

We fear that Mr. Crampton has misunderstood several matters. It is quite evident that the periodic cleaning of the specimens may have had some influence on the rate of corrosion, but it was necessary to clean the samples in order to weigh them and thus measure the progress of corrosion. The authors realized that such cleaning would probably influence the rate of corrosion and took care to remove only loose scale or powdery material; we endeavored, however, to state fully all condi-

tions. Nothing has been gained in the attempt to correct our tables and figures. If the total loss in weight were desired, reference should have been made to Table 5, instead of trying to figure back from the rate of corrosion given in Table 4.

The failure of tubes by corrosion may be the result of uniform solution, either regular or irregular (pitting), or the selective solution of one or more constituents (in this case dezinkification). Irregular solution or pitting may result from a number of conditions. The cause of the irregularity is frequently obscure and we are not ready to attempt judgment of the resistance of metal to corrosion by the depth of the deepest pit.

Apparently the presence of lead in brass, at least in small amounts, *i. e.*, approximately 0.5 per cent., does not greatly affect the rate of corrosion.

In the present investigation results are somewhat contradictory. In case of the tubes that Mr. Crampton picked out to substantiate his point of view., the leaded metal seems to have been acted upon somewhat more uniformly than that which did not contain lead. In the plate samples (Table 5) the leaded metal lost 0.1858 gm. by solution, while brass of the same composition but without lead lost 0.1583 gm.; a difference of approximately 17 per cent. in favor of the brass without lead. This is the only really quantitative result showing the relative corrosion of brass, with and without lead, that was obtained in this investigation.

Coatings Formed on Corroded Metals and Alloys *

By George M. Enos,† Met. E., Cincinnati, Ohio, and Robert J. Anderson,‡ Met. E., Boston Mass.

(Milwaukee Meeting, § October, 1924)

An important factor affecting the rate and nature of corrosion of metals and alloys is the film, or coating, formed on the surface; and this may accelerate or retard corrosive action once started. The formation of films and coatings is intimately associated with the chemical composition and physical constitution of both the metal and the corroding medium. A film or coating may be either the corrosion product resulting from oxidation; that is, an oxide or salt, or a deposition of suspended matter from the corroding media upon the surface of the metal, or a mixture of both. The coating may adhere tightly or loosely to the surface of the corroded metal. In short, a film or coating is the reaction product of the corroding medium and the metal, which adheres to the surface of the metal and with which may be intermingled material from the attacking media not concerned in the chemical reactions.

As the terms film and coating are used by different writers for very different things, distinction is made between the two, by the present writers, on the basis of thickness. Thus, a film is defined as a corrosion product or deposition, on the surface of a corroded metal, that is of such thickness that it cannot be measured by the metallurgical microscope. A coating, on the other hand, is of such thickness that it can be measured. If the resolving power of the 2-mm. (equivalent focal length) apochromatic oil immersion objective (N.A. 1.4) is taken as the limit of the microscope, the limiting resolution is two lines that are 0.0002 to 0.0004 mm. apart. It is thus possible to measure coatings that are greater than 0.0002 to 0.0004 mm. thick. This thickness is equivalent to 50,000–

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‡ Consulting Metallurgical Engineer.

§ Fall meeting Institute of Metals Division.

150,000 atom diameters or 0.2–0.4$\mu\mu$, and a film may be regarded as being of the order of say 0.3$\mu\mu$ thick, or less. A film may be gaseous, whereas a coating will necessarily be a liquid or solid.

In recent investigations on the corrosion of metals and alloys in acid mine waters,[1] microscopic examination was made of the nature and characteristics of the coatings formed in order to determine what kinds of coatings inhibit and what accelerate corrosion.

Nature of Coatings

It is known that the coating formed is an important variable in determining the rate. As indicated, coatings are formed from interaction of the corroding medium and the metal, or from deposition from the medium of material in solution or suspension, or from both in particular cases. Thus, a coating formed in atmospheric corrosion might consist of metallic oxides and hydroxides, mixed with soot, dust, etc. The chemical composition of the coating depends on the composition of the metal and of the corroding medium, while the physical structure of the coating depends, in part at least, on the physical condition of the metal surface. Thus, a coating may be loose and flocculent, or it may be hard and compact and adhere tightly to the corroded surface. The structure of the coating is important because flocculent or honeycomb structures will not retard corrosion as well as a compact structure.

While it is not proposed to deal at any length with films, it may be said that these may appear as faint tarnishes, causing dulling of a bright metal surface. The thin film of aluminum oxide formed on aluminum and its light alloys on exposure to the air and the bright temper colors formed on steel by oxidation may be cited.

Rust (hydrated ferric oxide) on iron and steel accelerates corrosion; Friend[2] has developed the auto-colloidal catalytic theory of corrosion which explains this accelerating effect; he has also shown that rust is colloidal in nature.

Wood[3] has discussed the nature of the colloids formed in the rusting of iron and has noted that it is the nature of the coating, particularly the

[1] W. A. Selvig and G. M. Enos: Corrosion Tests on Metals and Alloys in Acid Mine Waters from Coal Mines. *Bull.* 4, Coal-mining Investigations Series, Carnegie Institute of Technology, Pittsburgh (1922).

R. J. Anderson and G. M. Enos: Microstructural Aspects of Metals and Alloys Corroded by Acid Mine Water. *Bull.* 5, Coal-mining Investigation Series, Carnegie Institute of Technology, Pittsburgh (1923).

R. J. Anderson, G. M. Enos, and J. R. Adams: Accelerated Corrosion Testing of Metals and Alloys in Acid Mine Water. *Bull.* 6, Coal-mining Investigations, Carnegie Institute of Technology, Pittsburgh (1923).

[2] J. N. Friend: A New Theory of the Corrosion of Iron, *Trans.* Am. Electrochem. Soc. (1921) **40,** 63.

[3] J. K. Wood: Catalytic Action of Colloids in Corrosion. *Chem. & Met. Eng.,* (1923) **29,** 188.

flocculent state of the rust formed, that accelerates corrosion. He also notes that the rate of flow influences the corrosion rate, because at low velocities the oxygen concentration is increased and corrosion is increased, as explained by Friend. At the higher velocities, the catalytic hydrosols are washed away because the coating adheres so loosely, hence the corrosion rate is decreased.

The nature of the coatings formed, whether accelerating, retarding, or neutral to the corrosion rate, is worthy of much attention. Evans[4] has discussed the factors that govern the formation of protective coatings, and states that in cases where metals with basic oxides are rendered active by acids and passive by alkalies, while those with acidic oxides tend to become passive in acids and active in alkalies, the invisible protective layer is in the nature of an oxide film, but this film is probably of atomic dimensions only. While his discussion applies largely to films (as defined by the writers), the same principles should govern the formation of thicker layers, which will accelerate or retard the corrosion rate.

It is not the purpose of this paper to discuss the function of colloids in the formation of coatings. The importance of colloids and their effect on coating formation has been stressed by Bengough and Stuart.[5] The writers have observed instances of coatings that acted as accelerators and of some that acted as inhibitors of corrosion in the case of metals and alloys corroded in acid mine waters. In a recent work on the electrolytic corrosion of Admiralty metal (70:29:1 copper-zinc-tin) in various electrolytes, the writers[6] have examined the nature of the coatings formed on brass of different grain size and have found that grain size has no effect on coating formation.

Experiments on Coating Formation

In order to study the effect of the surface condition of alloys on coating formation, corrosion tests were made on a selected group of non-ferrous alloys in acid mine water. Duplicate test samples of various compositions, with one set of a given composition in the as-cast or as-rolled condition and the other set of corresponding composition machined or polished, were immersed in flowing acid mine water, as in previous tests by W. A. Selvig and one of the writers.[7] Eight alloys were selected for test, and included materials known to form thick coatings on the basis of previous work. The materials chosen for test are non-ferrous, hence

[4] U. R. Evans: Passivity and Overpotential. *Trans.* Faraday Soc. (1922) **18**, 1.

[5] G. D. Bengough and J. M. Stuart: The Nature of Corrosive Action, and the Function of Colloids in Corrosion, with an appendix of terms used in colloid chemistry. Sixth Report to the Corrosion Research Committee of the Institute of Metals. *Jnl.* Inst. of Metals (1922) **28**, 31.

[6] R. J. Anderson and G. M. Enos: Corrosion of Brass as Affected by Grain Size. *Trans.* (1924) **70**, 391.

[7] W. A. Selvig and G. M. Enos: *Op. cit.*

the present report does not deal with mill scale, rust, or other factors frequently associated with the corrosion of iron. The results are not directly comparable with corrosion results on iron and steel. The "as-cast" and "as-rolled" samples were placed in the water in the form they were received from the manufacturer. Duplicates of the as-cast pieces were surfaced by machining, so as to remove the skin. These machined or surfaced pieces were 2 by 6 in. by ¼ in. thick. Only one rolled material was included (monel metal); this was surfaced, so as to

TABLE 1.—*Composition and Loss in Weight of Samples, As Cast and Machined, Exposed to Acid Mine Water*

Designation	Chemical Composition, Per Cent.		Days Immersed	Test Piece Number[a]	Area, Square Centimeters	Weight, Grams		Total Loss, Grams	Loss, Milligrams per Square Centimeter per 24 Hr.
						Before Immersion	After Immersion		
Cast leaded cupro-nickel	Cu	53.57		X 1	186.66	582.98	532.49	50.49	3.70
	Sn	0.56							
	Ni	25.30	73	1	206.79	739.86	688.14	51.72	3.42
	Fe	0.61							
	Pb	19.58							
Cast chromium-iron-cupro-nickel	Cu	42.24		X 4	181.75	517.73	453.85	63.88	4.81
	Cr	11.89							
	Ni	35.00	73	4	203.95	630.35	561.38	68.97	4.63
	Si	1.50							
	Fe	9.35							
Rolled monel metal	Ni	65.1		X 40	164.07	114.57	88 38	26.19	3.54
	Cu	30.52	45						
	Fe	4.2		41	158.85	107.98	83.56	24.42	3.41
Cast lead-zinc bronze	Cu	86.34		X 73	172.22	342.64	319.73	22.91	1.82
	Pb	0.83	73						
	Sn	11.24		74	181.82	411.94	387.34	24.60	1.84
	Zn	1.60							
Cast aluminium bronze	Cu	93.9		X 76	162.91	250.83	227.41	23.42	1.96
	Al	6.1	73						
				76	175.10	342.98	326.25	16.73	1.30
Cast bronze	Cu	89.8		X 79	168.40	318.88	294.58	24.30	1.97
	Sn	9.7	73						
	Pb	0.5		80	181.04	410.75	389.66	21.09	1.59
Cast lead bronze	Cu	87.5		X 82	174.53	379.83	358.27	21.56	1.69
	Sn	10.6	73						
	Fe	1.6		83	180.01	440.56	415.38	25.18	1.90
Cast lead bronze	Cu	74.9		X 85	178.27	418.43	391.17	27.26	2.09
	Sn	10.5	73						
	Pb	14.3		86	202.59	674.79	648.05	26.74	1.81

[a] Numbers with prefix X denote machined or polished samples; numbers without prefix are as-cast or as-rolled samples.

remove the rolled skin, by rubbing with emery paper followed by buffing, instead of being machined. The rolled material was 2 by 6 in. by No. 16 gage (B. & S.).

The samples were placed in test racks and immersed in flowing mine water at the Edna No. 2 mine of the Hillman Coal & Coke Co., at Wendel, Westmoreland County, Pa. The average free acidity of the

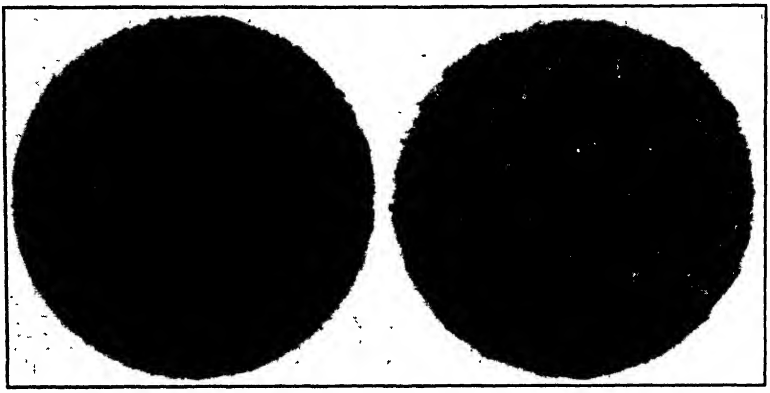


Fig. 1.—Sample X 1. Fig. 2.—Sample 1.

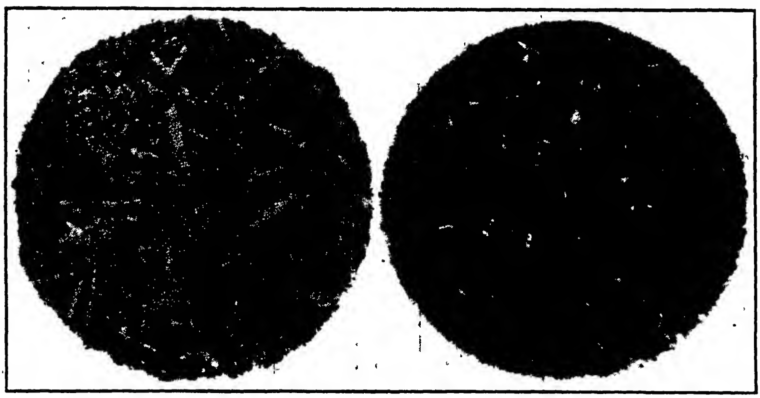


Fig. 3.—Sample X 4. Fig. 4.—Sample 4.

Microstructure of coatings; all taken on surfaces of corroded samples.

water was 2080 p.p.m. (sulfuric acid) and the average total acidity was 9570 p.p.m. (sulfuric acid plus sulfates of iron and aluminium). The flow of the water was regulated to 1.8 in. per min. Inspections of the samples and analyses of the water were made at frequent intervals. All of the samples except the monel metal were immersed for 73 days.

Table 1 is a summary giving the corrosion losses of the various alloys tested, including the test-piece numbers, designation, chemical composition, time of exposure, total loss in weight, and loss in weight

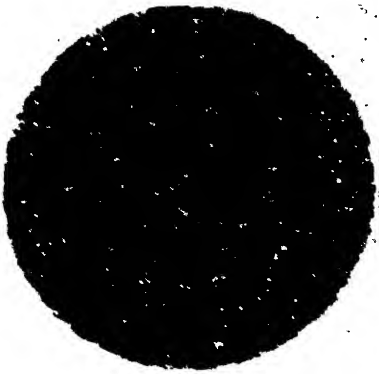


FIG. 5.—SAMPLE X 40.

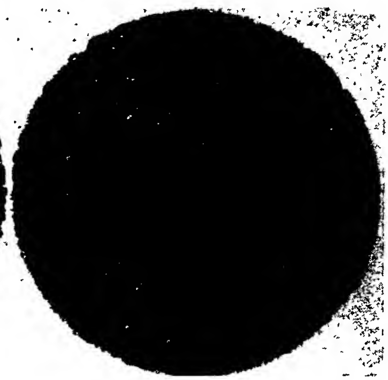


FIG. 6.—SAMPLE 41.

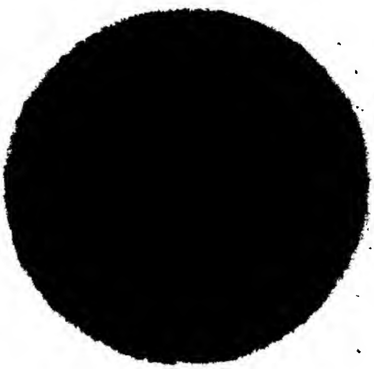


FIG. 7.—SAMPLE X 73.

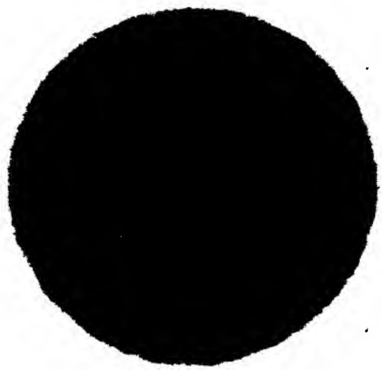


FIG. 8.—SAMPLE 74.

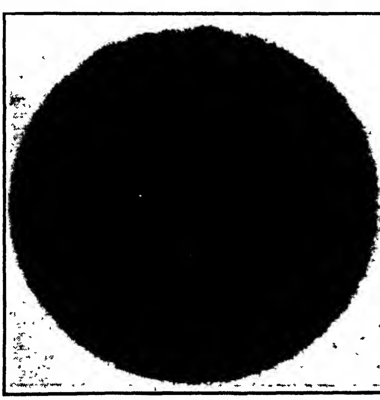


FIG. 9.—SAMPLE X 76.

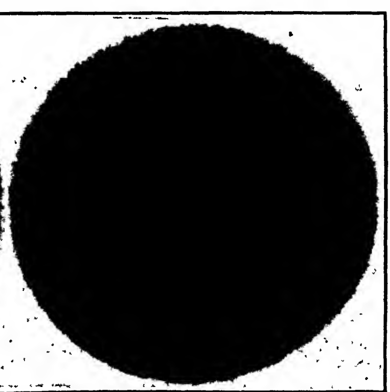
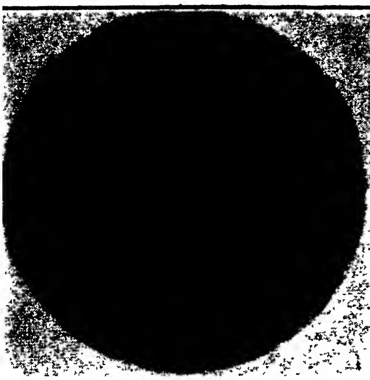


FIG. 10.—SAMPLE 76.

MICROSTRUCTURES OF COATINGS; ALL TAKEN ON SURFACES OF CORRODED SAMPLES.



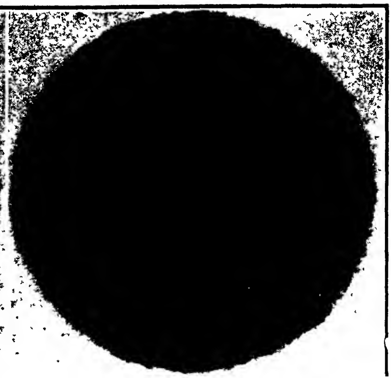
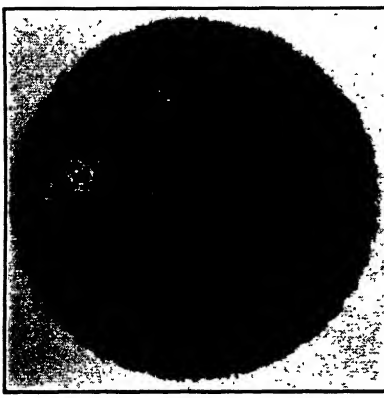


Fig. 11.—Sample X 79.

Fig. 12.—Sample 80.



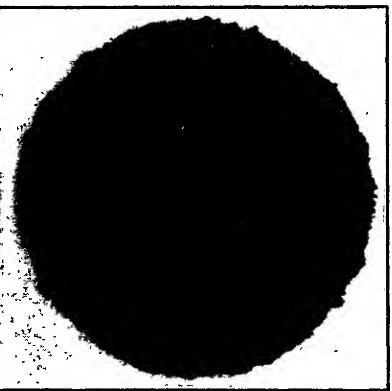
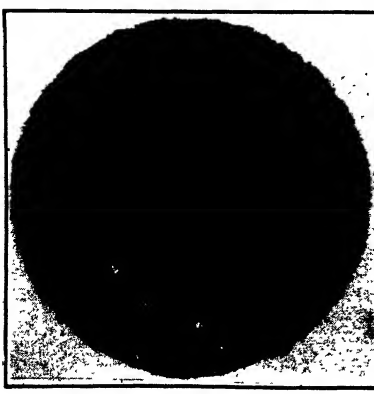


Fig. 13.—Sample X 82.

Fig. 14.—Sample 83.



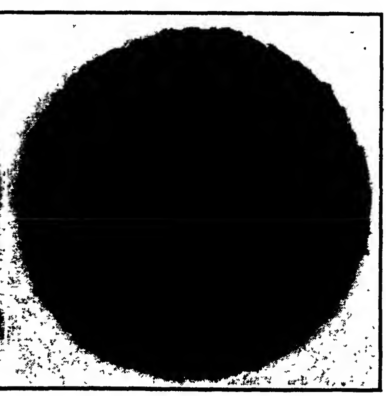


Fig. 15.—Sample X 85.

Fig. 16.—Sample 86.

Microstructure of coatings; all taken on surfaces of corroded samples.

expressed in milligrams per square centimeter per 24 hr. Table 2 gives the appearance of the coatings formed on the samples after slow drying (24 hr. at 105° C.), when examined under a binocular microscope at low magnifications and also the observations on the hardness of the coatings. The structures of the coatings are shown in Figs. 1 to 16; these photomicrographs were all made with oblique illumination at a magnification of 25 diameters.

TABLE 2.—*Nature of Coatings Formed on Samples Exposed to Acid Mine Water, as Shown by Visual Examination and Examination with Binocular Microscope at Low Magnifications*

Test Piece Number	Description of Coating
X 1	Soft coating, thick, gray color; honeycomb appearance.
1	Surface irregularly pitted; pit walls had honeycomb appearance.
X 4	Black-gray, needlelike, crystalline coating; thick and soft.
4	Same.
X 40	Black, flaky coating, adhering tightly; uniform pitting of surface.
40	Same, but coating did not adhere so tightly.
X 73	Green-gray, irridescent coating; hard and brittle; machine marks showed. Under the coating, corroded surface was grooved corresponding to machined surface.
74	Gray, hard, brittle coating.
X 76	Thin, brown coating; machine marks visible beneath.
76	Thin gray-green coating; very slight visible action.
X 79	Smooth, gray coating, containing cracks; material soft and granular.
80	Gray coating, soft and granular; original structure, pits, etc. left as cast.
X 82	Gray coating; machine marks showed; cracks in coating; material soft and granular.
83	Soft, loose, gray coating, appearing as cast.
X 85	Hard, thin, gray coating; machine marks showed.
86	Hard, thin, gray coating, appearing as cast.

In the previous long-time immersion tests,[8] in the course of the examinations made at mines during the duration of the tests, the loosely adhering coatings were removed from the test pieces by rubbing with the hand in water; that is, the pieces were cleaned as well as possible each time an examination was made, without using chemicals or extensive mechanical abrasion. In the present tests, the coatings were not disturbed during the exposure period. After microscopic examination had been made, the samples were soaked in distilled water for a few minutes and then cleaned in water with a fiber brush. They were then dried and weighed and the loss in weight determined. The same kinds of coatings

[8] W. A. Selvig and G. M. Enos: *Op. cit.*

are formed in the alloys when run in the accelerated electrolytic corrosion test using acid mine water as the electrolyte.[9]

In Table 1, in only one instance (cast aluminium bronze, X 76, 76) is there wide divergence between the loss for the as-cast and the machined samples. The loss data as recorded for the separate alloys check as well as did the loss data for the machined samples in the previous long-time immersion tests. The divergence in the case of the aluminium bronze is not large enough to suggest that the machining was responsible for the higher loss of test piece No. X 76 over No. 76. It appears, therefore, that the condition of the surface prior to immersion, whether machined or as cast, is not an important factor as regards relative corrosion, at least in mine water.

Summary

1. Coatings and films formed as corrosion products on metals and alloys have been defined, examined, and discussed.

2. The condition of the surface of the alloys examined, whether as cast or machined, apparently has little effect on the corrosion rate in mine water.

DISCUSSION

George K. Elliott, Cincinnati, Ohio.—The second paragraph of the summary "that the condition of the surface of the alloys examined, whether as-cast or machined, apparently has little effect on the corrosion rate in mine water," does not seem to hold good in other corroding media with which I am acquainted. Bronze with a roughly machined surface tested in distilled water will show considerable corrosion, while bronze with a finely polished surface will show no corrosion. There are many other examples where the surface has considerable influence on the amount of corrosion. It is interesting to know that the condition of the surface seems to have no effect on the corrosion rate in the case of mine water.

M. F. Sayre, Schenectady, N. Y.—In the case of aluminum, we have found that, in tests in salt spray, the difference between the corrosion of the cast surface and the machined surface is so little as to be negligible in comparison with the differences in rate for the various aluminum alloys themselves. This may be partly due to the facility with which an oxide layer forms on the machined aluminum surfaces. I have not had as much experience with some of the other alloys. If the test ran long enough, even with these, we might find that the corrosion would get underneath the surface skin, and once that happened there would probably be almost no difference in the rate between the cast and the machined surfaces.

[9] R. J. Anderson, G. M. Enos and J. R. Adams: *Op. cit.*

Samuel Daniels, Dayton, Ohio.—In regard to aluminum alloys, we have found that the surface as cast stood up better than the machined surface. Much depends sometimes on the way in which the test is conducted; for instance, whether the material is put in the salt spray, in distilled water, or in tap water or whether it is alternately immersed.

George K. Elliott.—In the case of some so-called stainless steels, it has been found that a highly buffed finish will corrode more readily than a finely ground finish. The supposition is that in this case a rather unstable equilibrium has been set up in the highly buffed surface which can be relieved by some form of ageing or mild annealing; in fact, after such treatment of the buffed pieces the difference did not exist.

D. Basch, Schenectady N. Y.—The statement that the polished surfaces stood up worse than the as-cast raises the question as to the kind of machined surface. If the surface showed scores, scratches, etc., there is no question that the machined surface would be worse than the as-cast.

With regard to stainless steel, a great deal depends on how the finish of the surface of the steel was obtained. If the surface was buffed in such a way that the individual particles on the surface were peened over, the full stainless characteristics of stainless steel are not obtained. If, on the other hand, great care is taken not to stress the surface particles in the polishing the resisting properties of the stainless steel will be fully realized.

Samuel Daniels.—The machined surfaces I mentioned were such as would ordinarily come from the machine shop and were not highly polished sections.

Experiments on the Heat Treatment of Alpha-Beta Brass*

By O. W. Ellis, M.Sc., and D. A. Schemnitz, M.A.Sc., Toronto, Ont.

(Milwaukee Meeting,† October, 1924)

Certain alloys[1] that, as a result of quenching, are retained in the form of homogeneous solid solution are known to increase in hardness and strength on standing at room temperature or on heating at slightly elevated temperatures. Other alloys[2] that, on rapid cooling, are held in the form of homogeneous solid solution, as, for example, certain steels, behave in like manner on heating to somewhat higher temperatures. The observed increase in the hardness and strength of these alloys, referred to as "aging" or as "secondary hardness," is widely accepted as being occasioned, either in whole or in part, by the precipitation in submicroscopic form of such constituents as were held in supersaturated solid solution as a result of cooling in excess of a certain critical rate.

In earlier discussions of the cause of age hardening or secondary hardness, the question of the hardness of the precipitated particles does not appear to have been raised. At present, however, the general opinion appears to be that age hardening and secondary hardness are occasioned by the precipitation of *hard* particles within the supersaturated solid substance.[3]

The authors may be wrong in their belief that the last is a prevailing opinion. Nevertheless, it is thought that the following experiments,

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* Communication from Department of Metallurgical Engineering of the University of Toronto.

† Fall meeting Institute of Metals Division.

[1] Wilm, *Metallurgie* (1911), 225; Jeffries, *Jnl.* Inst. of Metals (1919) **22**, 239; Merica, Waltenberg, and Scott, *Trans.* (1920) **64**, 41; Fraenkel and Send, *Ztschr. f. Metall.* (1920) **12**, 225; Rosenhain, Archbutt, and Hanson, Inst. Mech. Eng., Eleventh Report to the Alloys Research Committee (1921), etc.

[2] Scott, *Trans.* Am. Soc. Steel Treat. (June, 1921), 511; Bain, *Trans.* Am. Soc. Steel Treat. (Jan., 1924), 89.

[3] See, for example, the remarks of Jeffries and Archer, *Trans.* Am. Soc. Steel Treat. (1923) **4**, 283: "It is postulated that the increase in hardness of freshly quenched martensite on standing at room temperature or after mild tempering is due to the precipitation of cementite, the *hard* cementite particles 'keying' the slip planes of ferrite grains." This statement, of course, cannot be taken as representing the sentiment of these authors in respect of all types of "aging" and of "secondary hardness." [Italics are the authors'.]

which were carried out mainly with the view of determining whether the precipitation of *soft* particles within a supersaturated solid solution would not enhance its hardness, should be of interest.

Effect of Reheating Quenched Alpha-beta Brass on Its Microstructure

The question whether the reheating of true alpha-beta brasses[4] quenched from such temperatures and at such rates as to obtain homogeneous beta solid solution would result in mechanical improvement was taken up by one of the authors in 1918–19. The results of preliminary experiments did not encourage him to proceed with the investigation, it being noted that a structural arrangement likely to cause mechanical weakness was always obtained. This structural arrangement is shown in Figs. 1 and 2, which are photomicrographs of sections of two brasses which, prior to reheating at 400° C. for 40 hr., were in the form of homogeneous beta crystals. In both sections, it will be noted, excess alpha has been deposited, not only within the crystals, but at the crystal boundaries. Stead and Stedman[5] have clearly shown that this structural arrangement conduces to mechanical weakness. This structural arrangement, it should be noted, was found in these alloys subsequent to annealing at 400° C. for periods of less than 1 hr. (see Table 8).

The deleterious effect on tensile strength that might have been expected to result from the production of such a structural arrangement as is shown in Figs. 1 and 2 has been fully confirmed by the tensile tests made in connection with the experiments herein described. The results of these tensile tests, Tables 2, 4, and 6, prove that, while the mechanical condition of the alpha-beta alloys may, under certain circumstances, be improved by heat treatment and even by quenching, the effects of such treatments as comprise quenching and reheating to temperatures below the $\alpha + \beta \rightarrow \beta$ transformation temperature are little short of disastrous.

But the tests herein recorded were not made to confirm the opinion that the reheating of quenched alpha-beta brass would be of no commercial value. They were made primarily because it was recognized that alpha-beta brass was an alloy that could be obtained in the form of a supersaturated solid solution wherein could be deposited, as a result of reheating, particles (alpha) actually softer than the solid solution (beta) in which they were generated.

Alloys Used in the Experiments

There were used in the experiments two alloys of the following compositions:

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[4] Brasses that contain both the alpha and beta constituents after reheating to 400° C. subsequent to quenching with the view of obtaining homogeneous data.

[5] *Jnl.* Inst. of Metals., (1914) **11**, 119.

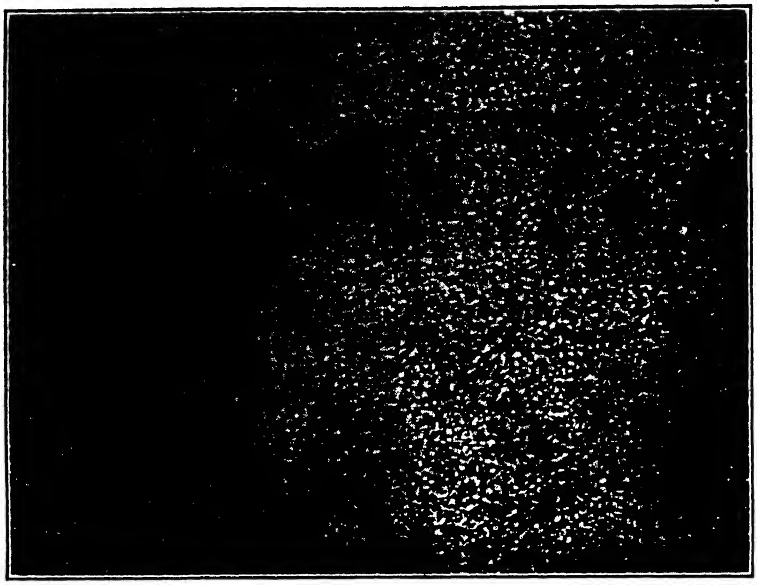

FIG. 1.—BRASS CONTAINING 57.40 PER CENT. COPPER; REHEATED SUBSEQUENT TO QUENCHING (700° C.) AT 400° C. FOR 40 HR.; ALPHA PRECIPITATED AT BETA BOUNDARIES. × 75.

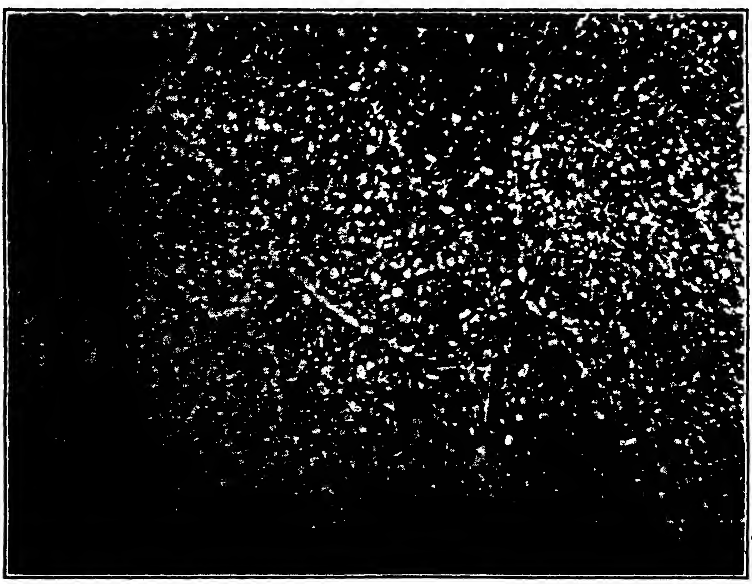

FIG. 2.—BRASS CONTAINING 56.51 PER CENT. COPPER; REHEATED SUBSEQUENT TO QUENCHING (700° C.) AT 400° C. FOR 40 HR., ALPHA PRECIPITATED AT BETA BOUNDARIES. × 75.

Alloy	A Per Cent.	B Per Cent.
Copper	56.66	52.02
Nickel	nil.	3.86
Zinc	difference	difference

which will be referred to throughout this paper as alloys A and B, respectively.

The alloys were in the form of chill castings, from which prismatic samples ½ by ½ by 3 in. were cut for purposes of test. These samples were annealed in bulk at a temperature of 725° to 750° C. for 1 hr. prior to other treatment. The mechanical properties of the alloys, subsequent to the preliminary anneal, were as follows:

	Alloy A	Alloy B
Maximum stress, lb. per sq. in.	54,100	51,200
Percentage elongation	39.5	32.2
Brinell hardness number	102	116

The test specimens used in making the mechanical tests were small, having gage lengths of only 1.155 in. and diameters of 0.326 in. The gage lengths of the specimens were four times the square roots of their cross-sectional areas. The Brinell tests were made with a 10-mm. ball and a load of 500 kg. It will be noted that in so far as their mechanical properties are concerned the annealed castings were of fair average quality.

By the expedient of quenching a number of small samples of the two alloys subsequent to their complete attainment to various temperatures, the $\alpha + \beta \rightarrow \beta$ transformation temperatures were approximately determined. For the pure brass, the transformation point under these conditions was found to be in the vicinity of 670° C. (under conditions of equilibrium the transformation point is lower); for the nickel brass it was found to be in the neighborhood of 720° C. The test samples for these experiments were, therefore, quenched in ice water from 720° C. and 770° C. (50° C. above the $\alpha + \beta \rightarrow \beta$ transformation temperature) respectively. Subsequent to quenching the samples were examined microscopically to confirm the absence of alpha.

Nature of Experiments

After quenching, the samples were reheated; some to 100° C., some to 200° C., some to 300° C., and some to 400° C. Prior to reheating, a determination of the Brinell hardness number of each sample was made. A similar determination was made after the thermal treatment and the percentage increase in hardness, if any, was then calculated. This method of estimating the observed increase in the hardness of the alloy seemed to be justified by the fact that the maximum variation from the average hardness number of the test samples prior to reheating was, in

both alloys, less than 3.0 per cent.; while the percentage increase in hardness as a result of reheating reached, in some instances, as high as 12.8 per cent.

Reheating of the test samples was conducted for time periods varying from ¼ to 40 hr. The samples were in all cases introduced into a furnace kept at the reheating temperature. They were then allowed to reach the temperature of the furnace, the time of reheating being measured from the time at which the samples first attained the temperature of the furnace.

Subsequent to reheating, the samples were thoroughly examined microscopically for traces of alpha. It was found in most cases extremely difficult to determine whether alpha had been precipitated at the boundaries of the beta grains, but it is certain that, in some instances, such precipitation had occurred when microscopic examination of both etched and unetched samples at high powers failed to reveal its presence. A variety of etching reagents was employed in this connection.

The samples were, in all cases, tested by the Brinell test and in some instances, in tension, by the usual methods of tensile test.

Results of Reheating Quenched Alpha-beta Brass at 100°, 200° and 300° C.

Reheating at 100° ± 2° C.

The reheating at 100° ± 2° C. was carried out in an electric drying oven thermostatically controlled; the results of the hardness tests and microscopic examinations made on the two series of samples are given in Table 1.

It should be noted that the authors think that in many cases alpha had been precipitated at the beta grain boundaries, though they were unable to detect its presence directly. The grain boundaries subsequent to etching always appeared as dark lines even when the samples were examined at high magnification. It was thought that this might be due to the fact that such light as arrived at the surface of the etched samples in the neighborhood of the boundaries was reflected away from the optical axis of the microscope. Many samples were, therefore, examined in the unetched state, but alpha could not be detected even under these conditions. The color of the fractures of the tensile test samples (Table 2), however, afforded indirect proof of this precipitation It can be stated with confidence that in no case had visible precipitation of alpha occurred within the beta crystals. The results of the tensile tests made on the two series of samples are recorded in Table 2.

Certain of the broken test specimens were characterized by what has been referred to, in the table, as a duplex fracture. The normal fracture of quenched alpha-beta brass is a dull brown-red. Certain of the above test specimens, however, possessed a coarsely crystalline

TABLE 1.—*Effect on Hardness of Reheating Quenched Samples of Alloys A and B at* 100° *C.*

Alloy	Brinell Hardness Numbers		Time of Reheating, Hours	Percentage Increase in Hardness	Structure Revealed by Microscope
	Prior to Reheating	Subsequent to Reheating			
A	136	136	¼	nil	Beta
	130	130	½	nil	
	133	133	1	nil	
	130	130	2	nil	
	136	138	4	1.5	
	136	143	6	5.1	
	130	143	8	10.0	
	133	150	16	12.8	
	130	146	32	12.3	
B	146	146	¼	nil	Beta
	150	150	½	nil	
	143	143	1	nil	
	143	143	2	nil	
	146	146	4	nil	
	146	146	6	nil	
	150	158	8	5.3	
	143	158	16	10.5	
	143	158	32	10.5	

TABLE 2.—*Effect on Tensile Strength of Reheating Quenched Samples of Alloys A and B at* 100° *C.*

Alloy	Condition of Sample	Time of Reheating, Hours	Tensile Strength, Pounds per Square Inch	Elongation, Per Cent.	Fracture
A	Quenched	nil	46,320	17.4	Dull brown red
	Reheated	6	46,700	13.0	Dull brown red
	Reheated	8	42,700	12.2	Dull brown red
	Reheated	16	49,360	20.0	Duplex
	Reheated	32	7,860	3.0	Duplex
B	Quenched	nil	45,150	Not noted	Dull brown red
	Reheated	6	6,600	2.6	Duplex
	Reheated	8	12,780	5.2	Duplex
	Reheated	16[a]			Duplex
	Reheated	32	14,040	2.0	Bright yellow

[a] Broken while being machined.

bright yellow fracture—the yellow approaching in tint that of the fracture of alpha brass of maximum zinc content. Others (those having a duplex fracture) had fractures wherein were exposed to view constituents having both the dull brown-red and the bright yellow. It has been assumed by the authors that the bright yellow of these fractures has been occasioned by precipitation of the alpha constituent at the grain boundaries, such bright yellow fractures having always been found in those samples reheated for long periods at 400° C., which showed clear microscopic evidence of the precipitation of alpha at the grain boundaries.

Whereas the presence of nickel retards the precipitation of the alpha constituent, it does not oppose the deleterious ultimate effect of that precipitation.

TABLE 3.—*Effect on Hardness of Reheating Quenched Samples of Alloys A and B at 200° C.*

Alloy	Brinell Hardness Numbers		Time of Reheating, Hours	Percentage Increase in Hardness	Structure Revealed by Microscope
	Prior to Reheating	Subsequent to Reheating			
	130	130	¼	nil	
	133	133	½	nil	
	133	133	1	nil	
	130	130	2	nil	Beta
A	133	133	4	nil	
	136	138	8	1.5	
	130	140	12	7.7	
	133	150	16	12.8	
	130	143	40	10.0	
	146	146	¼	nil	
	150	150	½	nil	
	150	150	1	nil	
	150	150	2	nil	
B	150	150	4	nil	Beta
	146	146	8	nil	
	146	152	12	4.1	
	146	158	16	8.2	
	150	158	40	5.3	

It is of interest, also, to note that reheating has reduced the ductility of the A alloy in certain cases, even though no evidence of the precipitation of alpha was observed either in the fracture of the test specimen or in etched sections of the same.

Reheating at 200° ± 10° *C.*

The reheating at 200° ± 10° C. was carried out in an electric-resistance crucible furnace, controlled by a variable external resistance. The

results of the hardness tests and microscopic examination made on the two series of samples are given in Table 3. The results of the tensile tests made on the two series of samples are recorded in Table 4.

The same remarks may be applied in respect of the results given in these tables as were applied to the results obtained with the samples reheated at 100° C.

TABLE 4.—*Effect on Tensile Strength of Reheating Quenched Samples of Alloys A and B at* 200° *C.*

Alloy	Condition of Sample	Time of Reheating, Hours	Tensile Strength, Pounds per Square Inch	Elongation, Per Cent.	Fracture
A	Quenched	nil	46,320	17.4	Dull brown-red
	Reheated	8	41,880	12.2	Duplex
	Reheated	12	49,300	21.7	Dull brown-red
	Reheated	16	38,370	6.1	Duplex
	Reheated	40	31,800	8.7	Duplex
B	Quenched	nil	45,500	Not noted	Dull brown-red
	Reheated	8[a]			Bright yellow
	Reheated	12	18,120	2.0	Bright yellow
	Reheated	16	5,580	4.3	Bright yellow
	Reheated	40[a]			Bright yellow

[a] Broken while being machined.

Reheating at 300° ± 10° C.

The reheating at 300° ± 10° C. was carried out in an electric-resistance crucible furnace, controlled by a variable external resistance. The results of the hardness tests and microscopic examination made on the two series of samples are given in Table 5. The results of the tensile tests made on the two series of alloys are recorded in Table 6.

In these experiments no doubt as to the precipitation of alpha existed, except in those samples that had been reheated for the shorter periods of time. In the case of these samples, however, the fractures of the tensile test specimens gave indirect evidence of the precipitation of alpha at the boundaries of the beta grains. This precipitation was such as to render the nickel alloy so fragile that it was impossible to turn samples for tensile test from the treated prisms.

AGING AT ROOM TEMPERATURE

To determine the effect of reheating the quenched alloys at 400° C., a series of samples of alloy A that had been quenched two weeks previously were taken for test. Before reheating at 400° C., the hardness numbers of the samples were checked, when it was found that the hardness had increased during the fortnight. The quenched simple brass is, there-

TABLE 5.—*Effect on Hardness of Reheating Quenched Samples of Alloys A and B at 300° C.*

Alloy	Brinell Hardness Numbers		Time of Reheating, Hours	Percentage Increase in Hardness	Structure Revealed by Microscope
	Prior to Reheating	Subsequent to Reheating			
A	133	136	¼	2.3	Beta
	133	138	½	3.8	Beta
	133	140	1	5.3	Beta + Alpha
	133	146	4	9.8	Beta + Alpha
	133	150	8	12.8	Beta + Alpha
	133	148	16	11.3	Beta + Alpha
	133	143	32	7.5	Beta + Alpha
	136	143	48	5.3	Beta + Alpha
B	143	150	¼	4.9	Beta
	143	152	½	6.3	Beta
	146	152	1	4.1	Beta
	150[a]	162	16	8.0	Beta + Alpha
	143	156	32	9.1	Beta + Alpha

[a] This anomalous result, the authors are unable to explain.

TABLE 6—*Effect on Tensile Strength of Reheating Quenched Samples of Alloys A and B at 300° C.*

Alloy	Condition of Sample	Time of Reheating, Hours	Tensile Strength, Pounds per Square Inch	Elongation, Per Cent.	Fracture
A	Quenched	nil	46,320	17.4	Dull brown red
	Reheated	½	27,480	4.3	Duplex
	Reheated	4	38,700	2.0	Duplex
	Reheated	8	33,600	4.3	Duplex
	Reheated	32	32,820	8.7	Duplex
B	Quenched	nil	45,500	Not noted	Dull brown red
	Reheated	1[a]			Bright yellow
	Reheated	16[a]			Bright yellow

[a] Broken while being machined.

fore, subject to "aging" in the most precise sense of this word. In Table 7 are given the results of the two series of tests made, the first immediately after quenching, the second two weeks later.

Reheating at 400 ± 10° *C.*

The samples were retreated subsequent to the second series of hardness tests; that is, they were requenched and then reheated to 400° C.

TABLE 7.—*Aging of Quenched Brass at Room Temperature*

Original Hardness Number	Hardness Number after Standing Two Weeks	Percentage Increase in Hardness
133	145	9.0
133	149	12.0
136	149	9.6
136	148	8.8
133	143	7.5
Average increase..........		9.4

TABLE 8.—*Effect of Reheating Quenched Samples of Alloy A at* 400° *C.*

Alloy	Brinell Hardness Numbers		Time of Reheating, Hours	Percentage Increase in Hardness	Structure Revealed by Microscope
	Prior to Reheating	Subsequent to Reheating			
A	136	148	nil[a]	8.8	Beta + Alpha
	133	143	¼	7.5	
	133	141	½	6.0	
	133	140	1	5.3	
	133	138	4	3.8	
	133	137	8	3.0	
	133	137	16	3.0	

[a] Sample heated until it just reached 400° C.

for various periods of time. The results of the hardness tests and microscopic examination made on the brass samples reheated at 400° C. are given in Table 8.

A definite loss in the percentage increase in hardness resulting from reheating was recorded for all periods of time in excess of that required to raise the alloy to 400° C., this simple treatment (mere heating to 400° C.) being, in itself, sufficient to cause precipitation of alpha. No tensile tests were made on these samples, it being considered unnecessary to carry the matter further in view of the poor results obtained as a result of reheating at the lower temperatures.

SUMMARY

By reheating alpha-beta brass, which as a result of quenching is retained at room temperature in the condition of homogeneous beta solid solution, it is possible to cause precipitation of alpha in submicroscopic form.

This precipitation of alpha has a deleterious influence on the tensile properties of the quenched brass, but has the effect of increasing the Brinell hardness of the material. This latter phenomenon is felt to be worthy of remark, as the precipitated alpha is appreciably softer than the

quenched beta wherein it is generated. It is well known that age hardening can be occasioned by the precipitation of hard particles (as in the case of duralumin); quenched brass, however, affords an example of a substance subject to age hardening caused by the precipitation of soft particles.

It is difficult to imagine how soft particles can act as "keys" to prevent the relative slip of the atom-bearing planes of a solid solution. If, however, it is postulated that the submicroscopic particles are of the nature of colloidal particles whose boundaries are controlled by surface tension and that at these boundaries there is distortion of the space lattices, both of the particles and of the surrounding solid solution, the increased resistance to the relative slip of the atom-bearing planes of the solid solution occasioned by the presence of the precipitated particles, whether they be hard or soft, can, it is thought, be explained.[6] The distortion of the space lattices at the boundaries of the particles referred to above opposes the propagation of slip via the slip planes of the precipitated substance. The hardness of the material wherein the precipitated substance is generated is therefore increased. The greater the number of such particles (particles whose boundaries are controlled by surface tension) the greater will be the strength of the alloy wherein they occur.

In the process of time, the forces of crystallization will exceed those surface-tension forces that control the boundaries of the particles and growth of the particles will proceed in accordance with the normal laws of crystallization. The spherical particles will change into minute allotriomorphic crystals at whose boundaries no space-lattice distortion will exist and which, therefore, will offer considerably less obstruction to the relative movement of adjacent atom-bearing planes of the matrix than is offered by the spherical particles, this diminution in the resistance offered to slip by the precipitated solute being due to the fact that slip in the matrix can be propagated with relative ease via the slip planes of the solute. A reduction in hardness will be the outcome of this change in the form of the precipitate.

To put it briefly: while spherical particles, whether soft or hard, are in process of formation the hardness of the alloy will increase, because of the increasing resistance offered to slip (owing to space lattice distortion at the boundaries of the particles) as a result of the precipitation of particles of this form. When the spherical particles begin to change into minute allotriomorphic crystals the hardness of the alloy will tend to decrease and will actually be lowered (1) when the rate of formation of allotriomorphic crystals exceeds the rate of formation of spherical particles and (2) as the allotriomorphic crystals themselves increase in size.

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[6] O. W. Ellis: The Structure of Metals. See report Winter Sectional Meeting of Am. Soc. Steel Treat., Rochester, *Iron Trade Rev.* (1924) **74,** 430.

DISCUSSION

WILLIAM H. BASSETT,* Waterbury, Conn.—Some authorities state that beta brass has no elongation. Probably the old idea for the weakness of this brass was due to the very thing that has been noted here—that is, the beta brass had alpha separations at the boundaries and consequently had very little strength.

When making the tensile tests, the author found that where he was unable to discover alpha microscopically, although the tests indicated it, the fractures were yellow between the grains; as the beta brass breaks with a brownish-red fracture, the author is warranted in his assumption that the yellow fracture was the result of the precipitation of alpha brass around the grain boundaries.

The paper gives the results of reheating quenched alpha-beta brass at 100°, 200°, and 300° C. At 100°, where he did not find, with the microscope, the presence of alpha, he shows that as the time of heating increases there is a decided increase in hardness in both samples, the one containing nickel being rather slow to show this increase.

The tensile-strength figures are interesting, because with the increased hardness, that is with the change taking place, the tensile strength and the elongation are greatly reduced. Similar results were obtained when the samples were heated to 200° and 300° C.

The conclusions are apparently in accordance with the ordinary theory of such cases. The practical application of this work is, perhaps, what we have already known—that if the heat treatment of beta brass causes the precipitation of alpha along the grain boundaries, the tensile properties of the material are ruined. It should not, however, be thought that the alpha-beta brasses are to be condemned on this account. The alpha-beta brasses in such material as naval brass, muntz metal, etc. are of the greatest use in the arts and have been for a long time. This paper rather shows what heat treatment should be avoided.

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The Hardness of Heat-treated Aluminum Bronze

By George F. Comstock,* Met. E., Niagara Falls, N. Y.

(Milwaukee Meeting,† October, 1924)

It has been known for many years that the alloy containing 90 per cent. copper and 10 per cent. aluminum can be hardened, like steel, by quenching from a suitable temperature, and that the hardened alloy can be softened again by annealing or drawing the temper. It does not seem to be generally appreciated, however, that the effect of the first slight reheating after quenching is actually increased hardness, the softening effect not taking place until a certain temperature of "drawing" has been exceeded. This paper gives the results of a few experiments on various specimens of cast 10 per cent. aluminum bronze, quenched for maximum hardness, and subsequently annealed at different temperatures. The hardness measurements were made with both a scleroscope and a standard Swedish Brinell machine; some peculiarities of the scleroscope test on this material are described.

The author is not aware of many previous investigations of the hardness of this alloy when quenched and drawn, but two important papers on the subject should be mentioned. The earliest was by Portevin and Arnou,[1] in which it was stated that tempering quenched 10 per cent. aluminum bronze at 400° C. increased the hardness as compared with the quenched untempered alloy and that reheating above that temperature was necessary to obtain any softening effect.

A later paper was by Seidell and Horvitz,[2] who mentioned Portevin and Arnou's work, but did not report any increase in hardness obtained

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[1] Sur le Revenu des Bronzes d'Aluminium. *Comptes Rendus* (1912) **8,** 511.

[2] Relation of Microstructure to Phase Changes in Heat-treated Aluminum Bronzes. *Chem. & Met. Eng.* (1919) **21,** 179.

by slight tempering after quenching. They agreed, however, that tempering to over 370° C. was necessary to soften the quenched alloy appreciably.

Neither paper reported any scleroscope tests; but as this instrument has been used commercially on heat-treated aluminum bronze, it was decided to investigate the hardness of quenched and tempered specimens by this means. The standard hammer was used throughout all this work, and the instrument was always kept in the usual fixed holder and not used either on the swing arm or freehand, as can be done if necessary.

The material experimented with was obtained in the form of tensile-test stubs, about ¾ in. in diameter and 2 or 3 in. long, from cast-to-size bars that had given good results in the tensile test. The alloy was 90 per cent. copper and 10 per cent. aluminum, made entirely from new metal of the best commercial quality, and without any flux or deoxidizer. The tensile-test results were about as follows:

Yield point..............	21,000 to 26,000 lb. per sq. in.
Tensile strength..........	65,000 to 75,000 lb. per sq. in.
Elongation in 2 in........	17 to 23 per cent.
Reduction of area.........	16 to 26 per cent.

The tensile-test stubs were heated gradually, in an electric muffle furnace, to 900° C., and held at that temperature for 20 to 30 min. They were then quenched as rapidly as possible in a large tank of cold running water. This treatment gave them a practically pure acicular beta structure, without any of the original alpha crystals remaining undissolved. In some parts of the samples, however, there was a slight precipitation of feathery alpha along the grain boundaries; it seems to be very difficult to quench rapidly enough in pure water to suppress this formation entirely. Flat strips about ¼ in. wide were prepared, with a fine file, on the curved surface of each quenched bar, and the scleroscope hardness was determined on that surface. The hardness as determined in this way was generally between 63 and 73 on the scleroscope scale. Some of the bars were quite uniform, but on most of them a range of from 3 to 8 points in hardness was found between one end of the filed strip and the other.

Four of these hardened bars, representing two heats of metal, were cut crosswise into disks about ¼ in. thick, for annealing or drawing the temper at various temperatures. This treatment was performed by first heating the muffle to the desired temperature, then inserting two of the hardened disks, one from each heat, bringing the temperature again to the desired point, holding it there for 20 min., and then cooling the disks in a box of lime. The temperatures were determined with a Leeds & Northrup potentiometer, using an iron-constantan thermocouple. The following day the disks were taken out of the lime, their surfaces were smoothed

for hardness tests, and one side of each was tested with the scleroscope and the other side later by the Brinell method. When making the Brinell tests, it was found that neither of the standard pressures, 500 or 3000 kg., were suitable for all the disks, as the lighter made too small a depression on the hard samples and the heavier made such a deep mark on the soft samples that there seemed to be danger of error from distortion or bulging of the small disks. A pressure of 1000 kg. was found suitable for the entire series, and all were tested at this load. The standard pressures were also used on some of the disks for comparison. A 10-mm. ball was used for all the Brinell tests; and the pressure was applied for 30 sec. in every test except those made with the 3000-kg. load, which was applied for only 15 sec. The results on these disks are given in Table 1. A range of values is given for the scleroscope tests, as numerous determinations were made with this instrument on each sample; abnormally low readings were disregarded.

TABLE 1.—*Hardness Numbers of Disks of Quenched* 10 *Per Cent. Aluminum Bronze, Reheated or Drawn at Various Temperatures*

Temperature of Reheating, Degrees C.	Scleroscope Number		Brinell Number, Heat A			Brinell Number, Heat H		
	Heat A	Heat H	3000-kg. Pressure	1000-kg. Pressure	500-kg. Pressure	3000-kg Pressure	1000-kg. Pressure	500-kg. Pressure
None	43–54	46–55	248	249	206	248	244	
150	48–55	56–58	241	249		235	238	
205	50–55	52–56	241	238		241	249	
260	53–57	53–58	262	260		255	249	
315	46–53	57–61	262	260		269	260	
400	49–60	56–62	262	260		269	260	
480	30–32	34–36	170	165		179	171	
565	23–27	23–26	163	159	136		159	143
650	21–22	22–24		133	124		138	130
760	19–20	19–20		121	100		121	109
870	18–19	20–21	131	113	100	134	117	109

The first line shows that the disks that were not reheated at all did not give as high scleroscope readings as the bars from which they were cut. This was supposed to have been caused by the concentration of the hardening effect of the quenching (or at least that part of the hardening effect which is revealed by the scleroscope) at the surface of the bar. The scleroscope tests on the flat strips filed on the entire bars were, of course, made nearer the quenched surface than the tests on the disks, which represented cross-sections of the bar. In subsequent work, therefore, the bars were cut for reheating into pieces about ¾ in. thick, and the scleroscope tests were made only on flat strips filed on the curved surface

that was the exterior of the bar when quenched. Almost as great a drop in hardness occurred, however, when the tests were made in this way, and it was proved, by repeated trials, that the scleroscope reading obtained from a hardened piece of 10 per cent. aluminum bronze was decreased from 5 to 15 points by simply cutting the piece in two. This was true whether the piece was merely quenched, or had been quenched and reheated slightly. Presumably the explanation is that the cutting

TABLE 2.—*Hardness Numbers of Specimens of Quenched* 10 *Per Cent. Aluminum Bronze, Reheated or Drawn at Low Temperatures*

Temperature of Reheating, Degrees C.	Scleroscope Tests on Flattened Surfaces		Brinell (3000-kg. Pressure)	
	Heat A	Heat F	Heat A, Cross-Sections	Heat F, Flattened Surfaces
None	55–59	58–61	255	269
150	54–57	55–59	248	277
205	54–57	56–61	241	269
260	55–58	59–61	269	277
315	52–55	57–61	262	286
345	54–57	58–62	262	286
370	48–52	55–58	277	286
400	48–50	50–53	269	269
425	36–39	42–44	196	255
455	25–27	38–42	183	223
480	21–24	29–31	179	202
510	20–22	26–28	170	196

reduced the scleroscope hardness by releasing internal stress acquired during the heat treatment. The Brinell readings were affected in a somewhat similar way, but any apparent softening after cutting in this case was probably due chiefly to cracking of the cut pieces under the heavy load used. This supports the belief that softening under these conditions is purely a stress effect, and not due to any structural change.

Table 1 shows that there was an appreciable increase in hardness, evidenced in both the scleroscope and Brinell tests, when these quenched specimens were reheated to temperatures between about 300° and 400° C. Between 400° and 480° C., softening began, and it was practically complete around 750° C. As the drawing temperatures used were not very close together around the critical point, near 400° C., another series of tests was made with temperatures chosen to give more data as to the exact point where maximum hardness was obtained. For this series, tensile-test stubs from two heats were quenched as before; they gave equally high scleroscope readings after quenching. The reheated pieces in this series, however, were about ¾ in. instead of ¼ in. thick; and as they were heat treated by the same method as the thinner pieces, they

undoubtedly cooled more slowly. The scleroscope tests on the drawn samples were made on strips about ¼ in. wide flattened by filing on the curved exterior surface of the bar. The Brinell tests were made similarly on samples from one heat, but on cross-sections of the samples from the

TABLE 3.—*Hardness Numbers of Larger Specimens of Quenched* 10 *Per Cent. Aluminum Bronze, Reheated to Low Temperatures and Cooled in Air and in Lime*

Temperature of Reheating, Degrees C.	Cooled in Air after Reheating		Cooled in Lime after Reheating	
	Scleroscope Number	Brinell Number, 1000-kg.	Scleroscope Number	Brinell Number, 1000-kg. Pressure
None	60–65		59–66	
150	62–66	249		
205			61–63	260
230	62–67	260		
260			60–63	244
315	62–66	285	65–70	278
345	63–70	279	60–64	272
370	60–66	255		
400	59–62	255		
425	48–55	205		

other heat, and with 3000 kg. pressure only. This heavy pressure was satisfactory for this series as most of the specimens were hard; it was thought that as the depressions were larger the tests would be somewhat more delicate than if made with a smaller load. Some of the hardest specimens, however, showed a tendency to crack under this heavy load.

Unfortunately, when the sections of heat A were cut it was found that most of these specimens were unsound. This was probably due to the type of pattern used in making the castings from which these test bars were machined. Thus the results from this series on heat A were perhaps not as reliable as might be desired. Judging from heat F, it would seem that the maximum hardness was attained after reheating to about 345° C., although there was not much softening until 400° C. was reached. In the earlier series, the maximum was found at 400° C.; softening commenced at this temperature in the second series, probably because the specimens in it were larger and cooled more slowly in the lime, so that the temperature of annealing affected the metal for a longer time. In heat A, the maximum Brinell reading was at 370° C. in this series, while the scleroscope did not show any increased reading in the reheated specimens. Presumably this was due to their unsoundness.

Another series of tests was made to investigate the difference in hardening effect produced by air cooling after quenching and reheating,

as compared to cooling in a heat-insulating material like lime. Entire tensile-test stubs were used in this series, the hardness tests being made on flat strips filed on the curved surfaces of the bars. Seven bars were quenched in water from 900° C. so as to give scleroscope readings of 60 to 65. They were reheated for 20 min. at the temperatures indicated in Table 3, and cooled in the air. After testing with the scleroscope and Brinell (using 1000-kg. load), the same specimens were quenched from 900° C.; four of them that gave scleroscope readings of 60 to 65 were

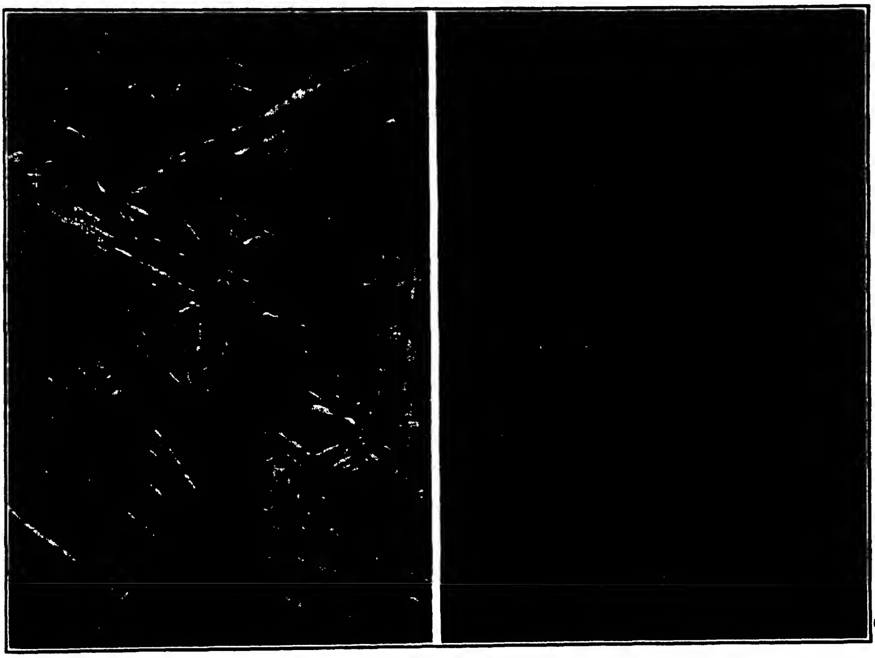

FIG. 1.—TYPICAL QUENCHED STRUCTURE WITH RATHER COARSE NEEDLES, AS SHOWN BY A SPECIMEN OF HEAT A, REHEATED TO 260° C.

FIG. 2.—SIMILAR STRUCTURE BUT FINER AND LESS DISTINCT, SHOWING THE CHANGE DUE TO REHEATING A SPECIMEN OF HEAT A TO 510° C.

FIGS. 1 TO 4 SHOW 10 PER CENT. ALUMINUM BRONZE QUENCHED IN WATER FROM 900° C. AND REHEATED TO DIFFERENT TEMPERATURES, ETCHED WITH ACID FERRIC CHLORIDE AND MAGNIFIED 200 DIAMETERS.

reheated as before but this time were cooled in lime. The results of hardness tests on the latter specimens are also reported in the table.

This series shows that the maximum hardness was developed by reheating to 315° C. when the final cooling was in lime, and by reheating to 315° or 345° C. when the final cooling was in air. Apparently the size of the piece treated had more influence on this point than whether the cooling was in lime or air, for these specimens were larger than those tested previously, which showed the maximum hardness when reheated at slightly higher temperatures. It is therefore important to realize that the

results quoted apply only to pieces of about the same size as ordinary tensile-test stubs (3/4 in. diameter and 2 or 3 in. long), or smaller. No experiments were made with larger pieces.

The microstructures of the disks used for the tests on heats A and H, results of which are given in Tables 1 and 2, were examined to see if the changes in hardness produced by reheating were accompanied by definite changes in structure. The etching reagent was an acidified ferric-chloride solution, as generally used for aluminum bronze. The increase

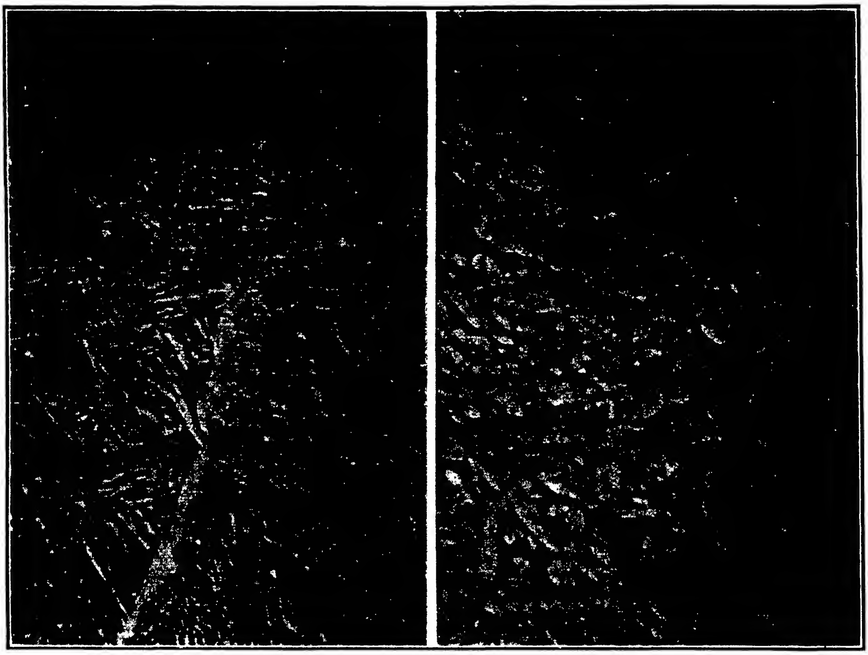

Fig. 3.—Structure of a specimen of heat H reheated to 650° C., showing fine alpha crystals instead of the acicular quenched structure.

Fig. 4.—Coarser alpha crystals in a specimen of heat H reheated to 760° C.

in hardness produced by slight reheating of the quenched specimens was found to be unaccompanied by any perceptible change in the microstructure. The first change noticed in the series of microsections, arranged in the order of increasing reheating temperatures, was an alteration in the color of the etched surface as viewed without the microscope. The specimens reheated at temperatures up to and including 400° C. had a yellowish color, while those reheated at higher temperatures were decidedly more red, up to about 800° C., where the structure reverted to the condition as cast and again became rather yellowish.

At about 500° C., there was an appreciable change in the microstructure toward the typical reheated form. The needles became finer,

more rounded, and much less distinct and contrasty; this was probably the result of the appearance of the alpha constituent in a recognizable form. At higher reheating temperatures, the alpha became more and more distinct and thicker until the alloy reached the completely softened state with a structure similar to that of the untreated casting. Figs. 1 to 4 illustrate these changes. The specimens having an acicular structure must not be overetched, for the number and size of the needles appearing on a given area of section may be much reduced by etching the specimen too deeply.

The scleroscope readings originally taken on the small disk samples at the beginning of this work seemed to vary more than they should, so tests were made on polished and etched specimens to see if the variations might not be due to actual differences in hardness between the large individual crystals exposed on the polished surface. At first some evidence pointing toward the correctness of this view was obtained, but later it was found that the trouble arose from improper support of the thin specimens in the holder at the base of the instrument. On only a few specimens were the polished surfaces exactly parallel with the reverse sides; when this condition did not occur, the clamp at the base of the scleroscope caused the upper face of the specimen to be perpendicular to the direction of the hammer blow, while the lower face was not. The anvil on which the specimen rested had such a broadly pointed top that the specimen did not always touch it directly below where the hammer fell, but contact was made off to one side when certain parts of the specimen were tested. Such conditions invariably gave a low reading, no matter how tightly the specimen was held in the clamp. This was remedied by placing a small bead of metal between the anvil and the specimen so that contact was secured between them exactly beneath the point where the hammer fell. The readings then obtained from a given specimen were fairly consistent and there were not a large number of abnormally low readings tobe discarded.

Summarizing the results of this work, it may be concluded that the scleroscope is not as reliable an instrument for measuring the hardness of quenched and tempered 10 per cent. aluminum bronze as the Brinell machine. Low scleroscope readings are obtained on such material if the quenched sample is merely cut into smaller pieces, or if the specimen tested is too thin and not perfectly supported in the instrument. Of course with the Brinell test, also a certain amount of care is required, and cracking of the hardened specimens must be avoided, but in general the conditions required for accurate results are easier to fulfil.

It was found that the maximum hardness was obtained, in small pieces of 10 per cent. aluminum bronze, not by quenching alone, but by quenching and reheating to from 315° to 370° C. Softening was produced by reheating above 370° or 400° C. and was practically complete

after reheating to 750° C. The reheating temperature giving the maximum hardness apparently depends somewhat on the rate of cooling, especially as determined by the size of the piece treated. A series of polished and etched microsections of this quenched alloy, reheated at different temperatures, showed a change to a more reddish color in the specimens that had been reheated above 400° C., but no appreciable change in microstructure until a reheating temperature of about 500° C. had been exceeded.

The author would acknowledge his indebtedness to the Buffalo Bronze Die Cast Corpn. for supplying the material for these experiments and the use of the Brinell machine, and also to the Titanium Alloy Mfg. Co. for the scleroscope and the metallographic equipment used.

DISCUSSION

Jesse Jones, East Pittsburgh, Pa.—Aluminum bronze is not a new alloy, but the difficulties of handling it in the foundry have retarded its application. The chief commercial application, possibly, is in the manufacture of gears for automobiles. One rather minor application is in complicated dies, especially when one part works upon another, for there is less wear and less liability of the parts to stick. Aluminum bronze also has an increasing application as an anti-acid metal.

The microstructures given on pages 811 and 812 are interesting; it would be interesting to know how the fine acicular structure shown in Fig. 2, would behave in a gear, whether it would have a greater life than the coarser structure shown in Fig. 4, and whether similar results would be obtained from an anti-acid standpoint.

One explanation of the variations in the scleroscope tests may be that in many cases where there is a coarsely crystalline structure, like the alpha shown in Fig. 4, the hammer possibly at one time strikes on a crystal that is considerably harder than some of the others. Of course, we try to obviate this variation by taking ten or more readings and averaging them. In the case of the Brinell test, the ball covers a large area and for that reason gives a better average hardness of a sample being tested.

Samuel Daniels, Dayton, Ohio.—We have investigated this alloy in the extruded form and have checked closely the Brinell hardness values for quenching and drawing given in Table 1.

We are experimenting with extruded 10 per cent. aluminum bronze for valve guides in aircraft engines. The main trouble with this material has been its lack of uniformity and the fact that it causes galling of the stem of the valve. Heat treatment tends to minimize the scoring but has no great effect on the wearing qualities. If the valve is so designed that the proportions of the head and stem are right and the cam mechanism is constructed so that there will be a minimum of side thrust,

aluminum bronze appears to be satisfactory in valve guides. In one 50-hr. engine test, cast-iron guides showed wear of from 0.017 to 0.030 in., whereas extruded 10 per cent. aluminum bronze, either as extruded or in the heat-treated condition, wore from nil to 0.002 in., maximum. Under the conditions just cited, this bronze wears better than cast iron and most of the other metals we have used, with the exception of hardened steel. The iron-bearing aluminum bronzes have not given good service. The only objections to 10 per cent. aluminum bronze in valve guides are its tendency to gall, its failure to ream readily, and its rather high cost, compared to cast iron.

ADOLPH BREGMAN, New York, N. Y.—Has anyone here had any experience with aluminum bronze as sand-cast? Practically all the gears are cast in permanent molds.

JESSE JONES.—I have not had any experience with the sand casting of this alloy, but a friend assures me that while the permanent-mold castings are much superior, so far as grain is concerned, there is no difficulty whatever in sand-casting alloys. In fact, he says that it is much more easily handled than manganese bronze, is more nearly fool-proof, and there is no difficulty whatever in handling it in a foundry after a reasonable amount of experience has been had. Very satisfactory results are obtained in sand casting.

GEORGE F. COMSTOCK (author's reply to discussion).—As to the wearing quality of the structure shown in Fig. 2, compared with the normal cast structure of this alloy, some rather crude rolling-abrasion tests carried out some years ago for the Titanium Bronze Co. showed decidedly better results for the heat-treated alloy than for the alloy as cast. The addition of 4 per cent. iron to the bronze, however, resulted in about the same improvement as the heat treatment without the iron.

This result is supported by L. Guillet[3] in an article describing tests of aluminum bronze with the Jannin wear-testing machine. He reported the best results after a quench and draw at 500° C., and very much worse results after drawing at 700° C. It remains to be seen whether this same comparison would hold true in the case of gears in actual service. The Buffalo Bronze Die Cast Corpn. has found that a modified composition is very effective in reducing the friction and wear of the aluminum-bronze gear when driven by a standard worm under heavy load.

I do not know how the acid resistance of the heat-treated bronze compares with that of the cast alloy, but see no reason to suppose that it would be any less.

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[3] *Rev. de Met.* (1922) **19**, 120.

Etching Aluminum and Its Alloys for Macroscopic and Microscopic Examination

By Fulton B. Flick,* New Kensington, Pa.

(New York Meeting, February, 1925)

The micrography and macrography of aluminum and its alloys present certain difficulties. Many of the difficulties attendant on the micrography have been removed by methods developed during the past few years, notably those of E. H. Dix, Jr.[1] The development of grain size in aluminum and its alloys may be equally troublesome, yet comparatively little detailed attention appears to have been given to it. Satisfactory reagents are available for the development of such structures in ferrous and most non-ferrous metals, but those applied to aluminum and its alloys, *i. e.*, alcoholic or aqueous solutions of sodium hydroxide or hydrofluoric acid are not entirely satisfactory. Hanson and Archbutt,[2] in speaking of these two reagents, state that "These two reagents give fairly satisfactory results, but they sometimes produce badly tarnished surfaces from which the surface deposit is difficult to remove."

It has been our experience that neither of these reagents is to be entirely relied on for developing structures suitable for study or photography. This means that when the etch fails to produce satisfactory results the specimen must be repolished, through the 000-paper at least, and then etched with another reagent. This procedure entails a considerable loss of time, and the final results may not be all that might be desired. However, the reagent to be described, although not a panacea for all etching troubles, has improved results so markedly that it is felt that it is worth offering as a grain-size etch generally applicable to aluminum and aluminum alloys.

Czochralski[3] in 1915 mentioned the application of a solution of 10 to 20 c. c. concentrated hydrofluoric acid in 100 c. c. absolute alcohol, etching in this reagent being followed by dipping in concentrated hydrochloric acid solution.

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[1] *Chem. & Met. Eng.* (1922) **27**, 2712.

[2] *Proc.* Inst. of Metals (1919) **21**, 291.

[3] *Stahl u. Eisen* (1915) **35**, 1073.

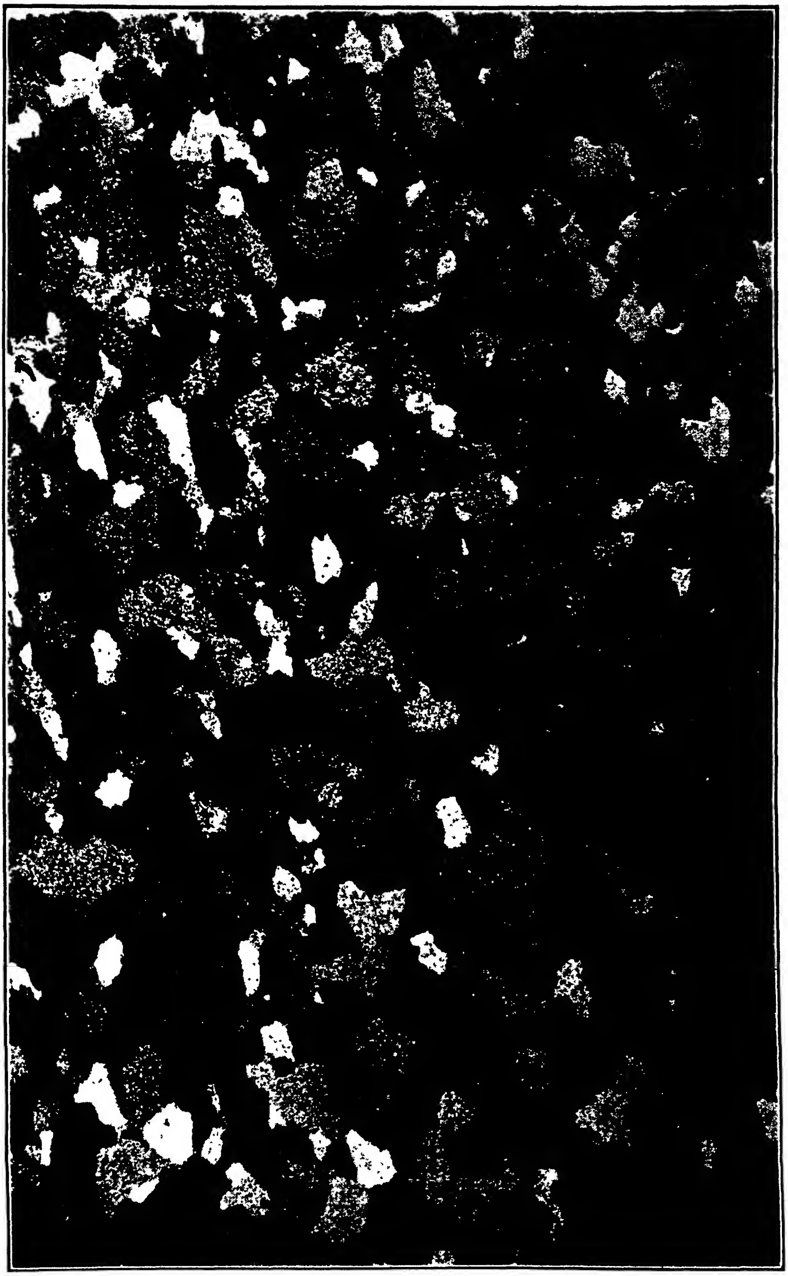


FIG. 1.—99.2 PER CENT. ANNEALED ALUMINUM SHEET ETCHED IN 8.7 PER CENT. HF-13 PER CENT. HCl. × 10.

Beyond mention in a few papers appearing in German scientific periodicals, this etch does not seem to have been studied to any great extent by aluminum metallographists. The excellence of results obtained

FIG. 2.—ETCHED IN 8.7 PER CENT. HF-13 PER CENT. HCl SOLUTION; ILLUSTRATES STRUCTURE DEVELOPED IN SPECIMEN TAKEN FROM CORNER OF INGOT OF MANGANESE-ALUMINUM ALLOY CONTAINING 1.20 PER CENT. MANGANESE; COPPER + IRON + SILICON 0.18 PER CENT., BALANCE ALUMINUM. × 5.

by using it, as shown by photographic reproduction, called our attention to it in the search for a reagent more generally applicable to development of structure.

Two disadvantages of such an etch are apparent at once. The first is the use of two solutions. This is an important condition in that it is time consuming and tarnish may form during transfer from one solution

FIG. 3.—ETCHED IN 8.7 PER CENT. HF-13 PER CENT. HCl SOLUTION; PORTRAYS SHAPE AND ARRANGEMENT OF GRAINS IN CROSS-SECTION OF NOTCH BAR POURED FROM 99.2 PER CENT. ALUMINUM. × 5.

to the other. The second disadvantage lies in the use of hydrochloric acid solution. As is so well known, this reagent attacks aluminum with such rapidity that, unless extreme care is taken, the attack may be so vigorous and deep that the structure will be spoiled.

Inasmuch as the use of one solution seemed desirable, a combination of hydrofluoric-hydrochloric acid solutions was experimented with, with most gratifying results. The solution finally adopted as standard consists of: 90 c. c. water, 10 c. c. concentrated hydrofluoric acid, 15 c. c. concentrated hydrochloric acid; this results in the following percentages by volume: 8.7 per cent. concentrated hydrofluoric acid solution, 13.0 per cent. concentrated hydrochloric acid solution.

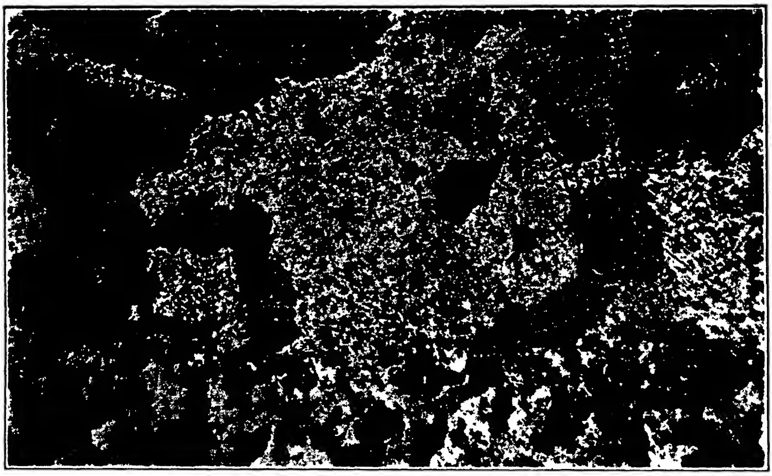
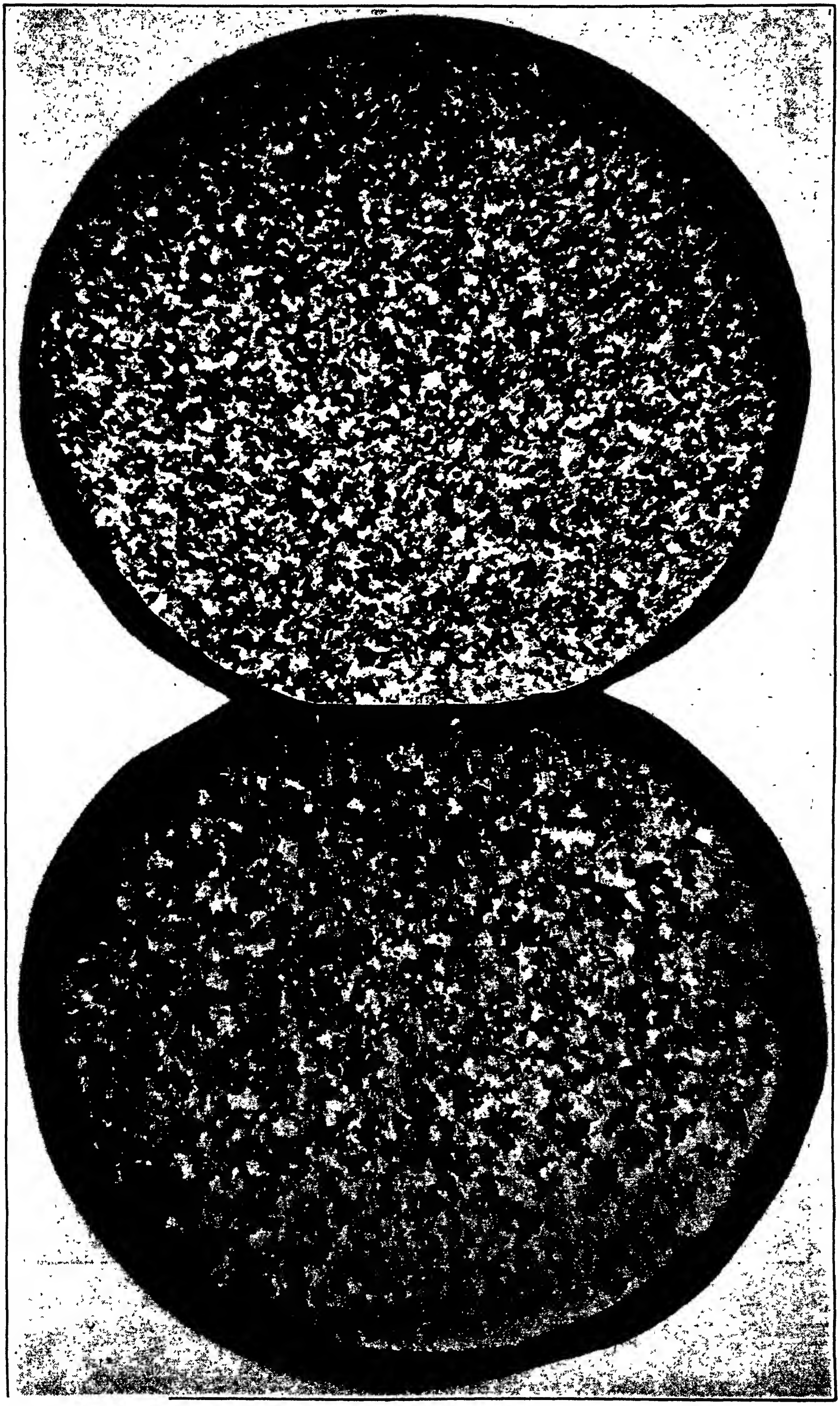


FIG. 4.—ETCHED IN 8.7 PER CENT. HF-13 PER CENT. HCl MIXTURE; ILLUSTRATES STRUCTURE DEVELOPED IN SPECIMEN CUT FROM INGOT OF STRONG ALUMINUM ALLOY TYPE; CHILLING EFFECT OF MOLD IS SHOWN BY CRYSTALS AT BOTTOM; NOTE PARTIAL DEVELOPMENT OF DENDRITIC STRUCTURES IN LARGER CRYSTALS IN INTERIOR OF INGOT. $\times$ 10.

The use of such a solution reveals the grain size of aluminum in an excellent manner, as illustrated in the accompanying macrographs. The specimen, cleaned by swabbing with alcohol if it is greasy, is immersed in the solution. If the specimen is too large, the solution may be poured over it and allowed to react for a few minutes. At short intervals, the piece is removed and washed with hot water, the structure is examined and the process repeated until the desired effect is obtained. In general, satisfactory etching requires from 30 to 90 sec. It is best to make up fresh solution each day, or after a number of specimens have been etched. To save time, a stock solution of hydrochloric acid may be made up and the appropriate amounts of hydrofluoric acid solution added to given volumes when the reagent is to be used.

Nichrome crucible tongs are used in this laboratory to hold the specimens. With most alloys, no after dip is necessary, except in the case of alloys containing copper, which become covered with a black coating during the etching. This coating is removed by immersion in concentrated nitric acid solution, which does not otherwise alter the



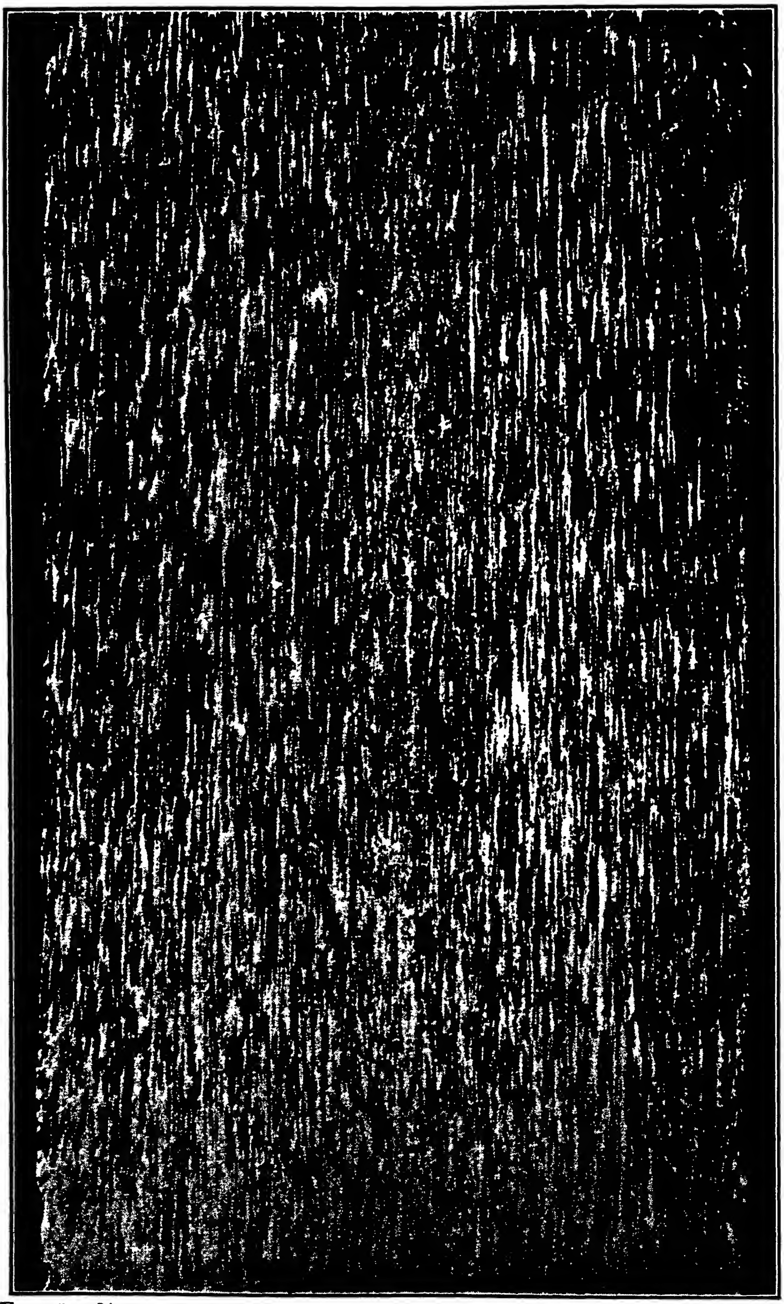


FIG. 6.—ETCHED IN 8.7 PER CENT. HF-13 PER CENT. HCl SOLUTION; SHOWS ELONGATED GRAINS IN CROSS-SECTION OF SPECIMEN CUT IN DIRECTION OF ROLLING FROM A 3/8-IN. HOT-ROLLED SLAB OF MANGANESE-ALUMINUM ALLOY. × 10.

results of the etch. Attempts to avoid the use of this after dip by combining the nitric acid with the hydrofluoric acid-hydrochloric acid solution were unsuccessful; the surface always lacks the characteristic brilliance of the hydrofluoric acid-hydrochloric acid-water etch.

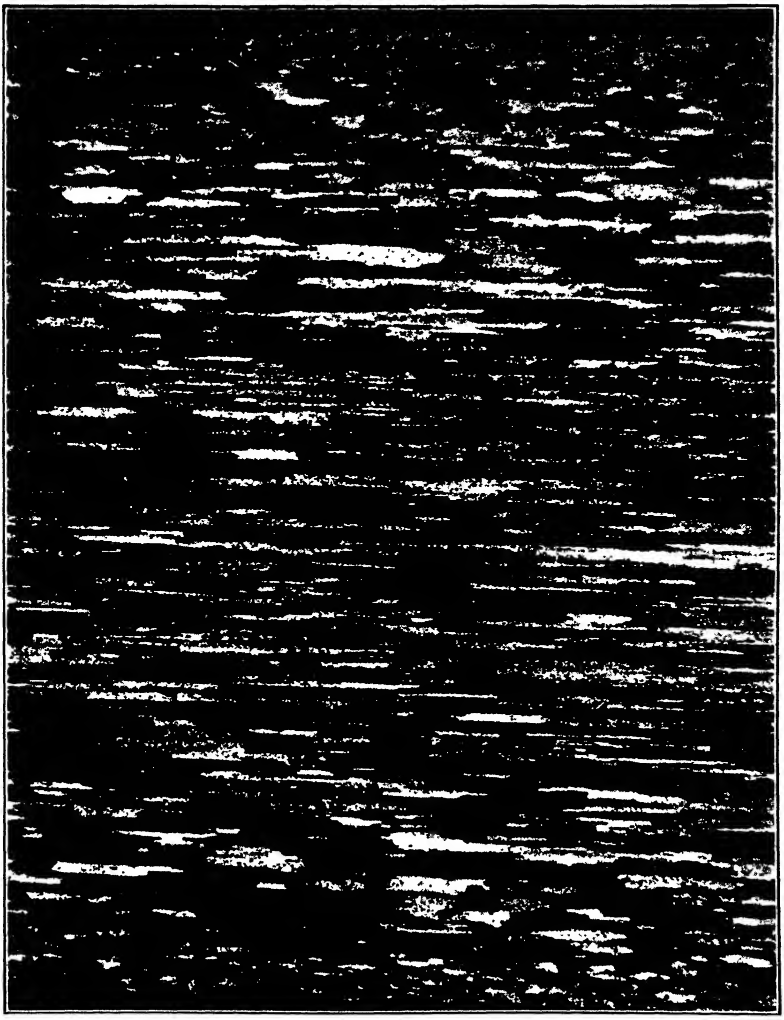


FIG. 7.—ETCHED IN 8.7 PER CENT. HF-13 PER CENT. HCl SOLUTION; SECTION ACROSS FLATS OF ½ IN. EXTRUDED HEXAGONAL ROD OF STRONG ALUMINUM ALLOY TYPE; SHOWS VARIATION IN GRAIN SIZE FROM EDGE TO EDGE OF ROD. × 10.

No claim is made that this etching procedure is applicable to all types of aluminum alloys in all conditions. It has been used, however, on a wide variety of alloys, cast, rolled and heat treated, with so much success that it has been concluded that it is more generally useful than

the etches hitherto commonly applied. Some of the results obtained are depicted in the accompanying illustrations, most of which require no detailed comment. They show, in general, how the brilliant and detailed results obtained may aid in the examination and study of various structures.

Fig. 1[4] illustrates the structure developed in a sheet of 99.2 per cent. aluminum, using the etch just described. The excellence of the result is apparent, both with regard to brilliance of the surface and excellence of the "oriented luster," which serve to make the contrast prominent.

The result could not be matched using 10 per cent. sodium hydroxide or by following Czochralski's[5] directions. With the former, only the faintest outline of grain structure could be produced, and by the latter method the sheet was tarnished so badly as to obscure the structure and to cause, at times, groups of grains to appear as one. The tarnish referred to has been mentioned by various investigators; it could not be removed chemically.

By first quickly dipping the sheet in concentrated hydrochloric acid followed by immersion in the alcoholic hydrofluoric acid solution and again dipping in hydrochloric acid, results were obtained which were quite comparable to those arising from the etch described in this paper. Even so, great care must be taken not to prolong the hydrochloric acid dip, or the tarnish forms. Furthermore, the use of alcoholic hydrofluoric acid solution prolongs considerably the necessary time of etching. Accordingly, it is felt that the etch just described is more nearly foolproof and of better general character than is that in which the hydrofluoric acid dip is followed by hydrochloric acid.

Mention should be made of the etching procedure developed by Carpenter and Elam[6] by which the specimen is immersed in an alcoholic solution of sodium hydroxide, water then being added drop by drop until fine bubbles indicate reaction; after etching in this solution the specimen is transferred to a very dilute solution of hydrofluoric acid (1 to 2 per cent. in water). The results obtained by use of this procedure were not very encouraging and could not compare with those produced by the hydrofluoric acid-hydrochloric acid etch.

Figs. 2 and 3 depict the structure developed in specimens cut from the corners of ingots and show the great brilliance and contrast produced, thus allowing a careful study of cast structures. Fig. 4 is representative of an ingot of the strong-alloy type. The sharply chilled region

[4] Figs. 1 to 8, inclusive, were taken using a Zeiss 75-mm. microplanar objective; carbon arc, oblique illumination; Wratten orange E-22 filter. Fig. 9 was taken with a Zeiss 35-mm. microplanar objective, using vertical illumination, the other conditions being the same.

[5] *Loc. cit.*

[6] *Proc.* Inst. of Metals (1920) **24,** 83.

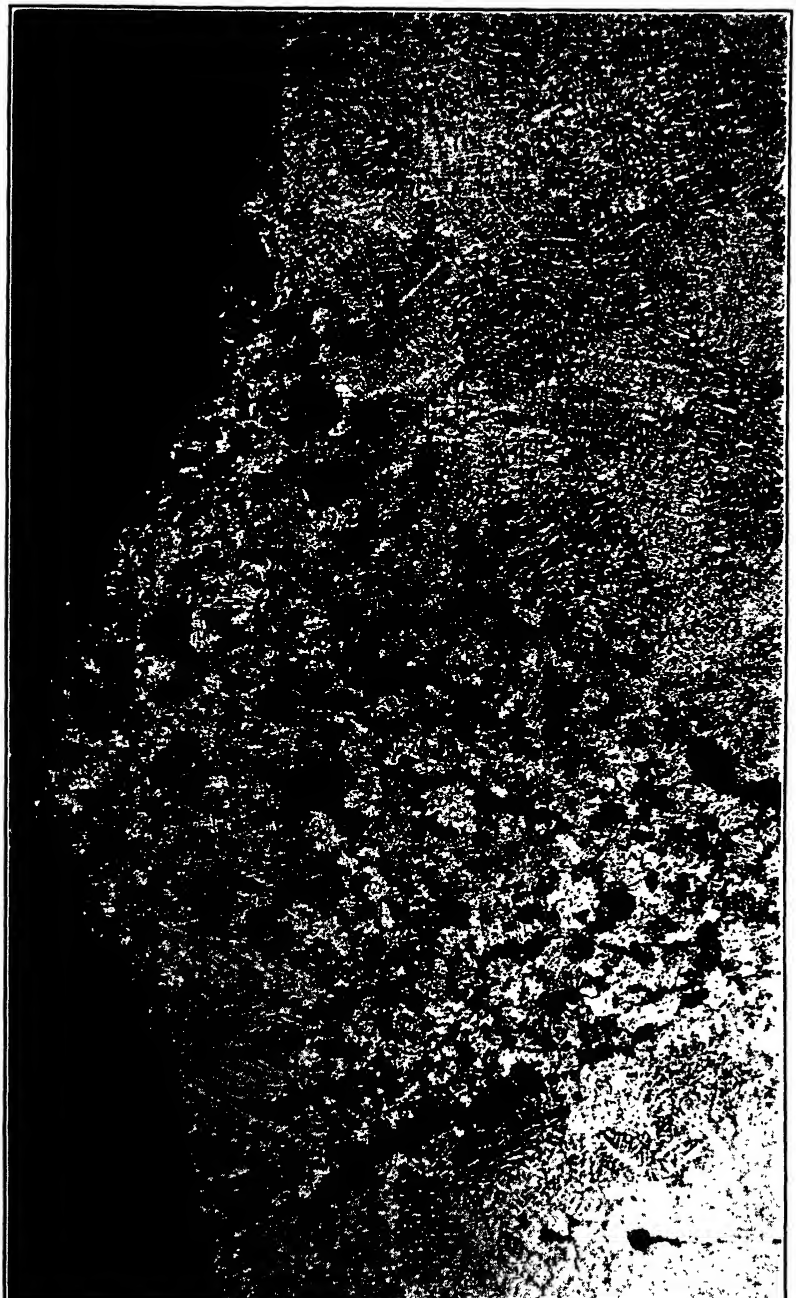


FIG. 8.—ETCHED IN 8.7 PER CENT. HF-13 PER CENT. HCl SOLUTION; TRANSVERSE SECTION THROUGH DEFECTIVE WELD IN 5 PER CENT. SILICON-ALUMINUM TEST BAR. ETCH DEVELOPED FOUR THINGS: BOUNDARY BETWEEN WELD AND BAR, CAVITIES BETWEEN BAR AND METAL OF WELD, GRAIN SIZE OF EDGE, START OF DEVELOPMENT OF DENDRITIC STRUCTURE IN GRAINS. × 10.

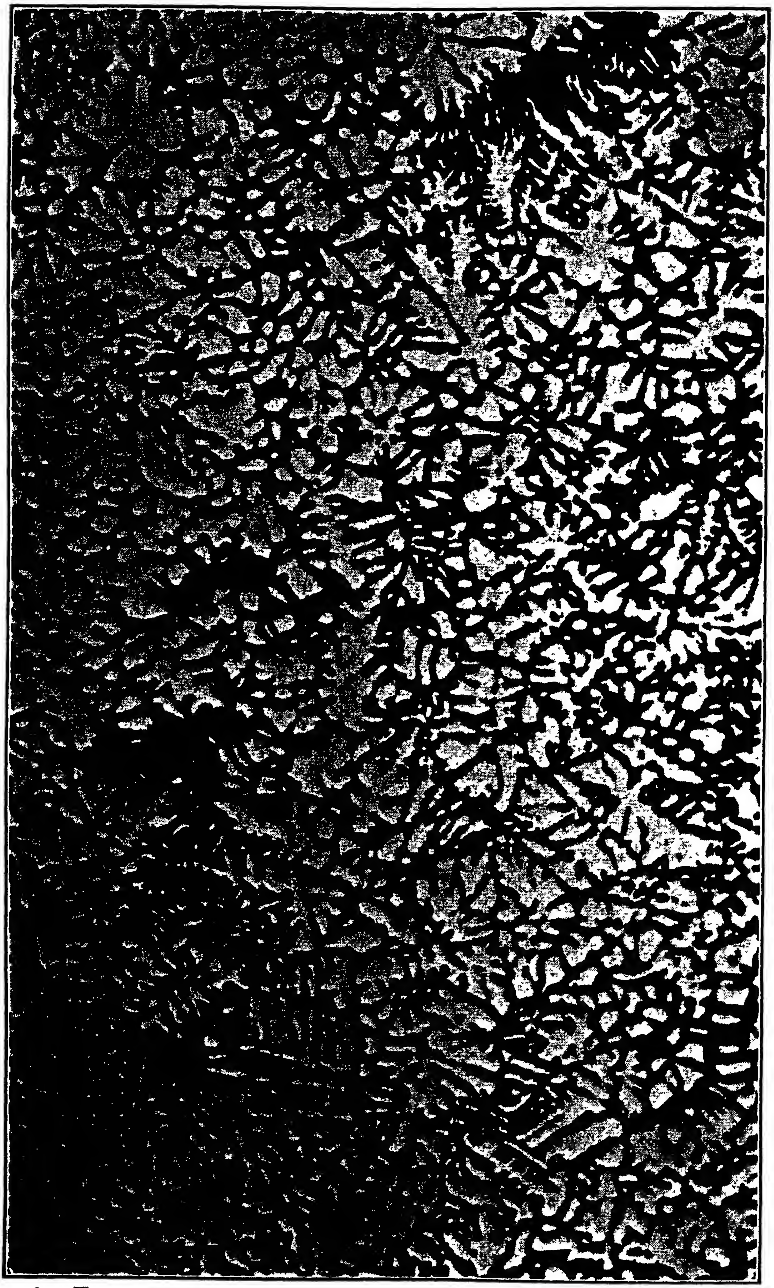


FIG. 9.—ETCHED IN 8.7 PER CENT. HF-13 PER CENT. HCl SOLUTION; SHOWS DENDRITIC STRUCTURE IN SPECIMEN CUT FROM INGOT OF FOLLOWING ANALYSIS: Mg 4.09 PER CENT., Cu + Fe + Si 0.44 PER CENT., BALANCE ALUMINUM. × 50.

due to the mold wall is readily recognizable; beyond, the larger grains are evident. Note should also be taken of the development of dendritic structure.

Fig. 5 illustrates the application of this etch to production studies. In this case one bar showed a considerably higher strength than did the other bar. Coarse etching revealed the disparity in grain size. Although this might not account entirely for the differences, it may give a clue as to the fundamental defect.

Figs. 6 and 7 show the results obtained with wrought material, which is in general the most difficult to etch successfully for grain structure. The application to rolling or extrusion studies is apparent.

Fig. 8 portrays the result obtained in etching a defective welded section in which the weld, cavities, and bar structures are clearly revealed. Fig. 9 illustrates the application of this etch in development of dendritic structures in aluminum-magnesium alloys.

Finally it should be pointed out that this reagent is equally applicable to etching for micro-examination, both for developing structure and for differentiation of constituents. Studies relating to the differentiation by etching of the various constituents met with in aluminum alloys are in progress in this laboratory, which will be reported in future papers.

The author wishes to express his indebtedness and thanks to Mr. Edgar H. Dix, Jr. for advice and criticism of this work and paper, together with his appreciation of valuable assistance of Mr. George W. Wilcox in the photography.

DISCUSSION

Samuel Daniels,* McCook Field, Dayton, Ohio (written discussion). The aqueous hydrofluoric acid-hydrochloric acid reagent recommended by the author is a valuable contribution to the study of aluminum and its alloys. Its function seems to be to reveal the size, shape, and orientation of the grains and of the hard constituents in aluminum alloys and not to aid particularly in distinguishing the nature of the compounds themselves.

Experiments on several sand-cast alloys have shown that the etching period varies with the composition and condition of the metal. For instance, the 92.5 per cent. aluminum, 4 per cent. copper, 2 per cent. nickel, and 1.5 per cent. magnesium alloy required only 5 sec. immersion in the author's solution to reveal the grain structure satisfactorily. Because of the vigorous action of the solution, it would appear advisable to move the specimen about in order to prevent the hydrogen from preventing action locally on the surface of the specimen.

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* Chief, Metals Branch, Materials Section, Engineering Division, War Dept. Air Service.

New Developments in High-strength Aluminum Alloys

By Robert S. Archer* and Zay Jeffries,† Cleveland, Ohio

(New York Meeting, February, 1925)

It is about fifteen years since the development in Germany, largely by Alfred Wilm, of the aluminum alloy called duralumin. In this alloy, combining as it does the tensile strength of mild steel with the lightness and corrosion resistance of aluminum, a distinctly new material was presented to the engineering world. Despite the evident usefulness of this material, however, its commercial development has been slow, due in part to the difficulties involved in its fabrication.

In view of the potentially great utility of strong aluminum alloys, it seemed desirable to find means of producing such alloys with better fabricating properties, and work was undertaken with this object in the laboratories of the Aluminum Company of America several years ago. This work has resulted in the production of two new types of aluminum alloy of the "strong alloy" class, having distinctly improved fabricating qualities. The knowledge gained has also made it possible to produce alloys of the duralumin type with greater strength and hardness than previously obtained. There have thus been made available some new engineering materials which it is the object of this paper to describe.

These alloys, including duralumin, are fundamentally wrought alloys. Castings of the same compositions heat treated in the same manner give inferior physical properties, particularly as to ductility. The statements made subsequently concerning properties and heat treatment apply to material that has received sufficient working to thoroughly break down the cast structure. The material referred to has, in general, undergone a reduction in section of at least 80 per cent. by mechanical working. It may be mentioned in passing that other compositions have been found that are suitable for the production of the maximum physical properties in heat-treated castings.

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* Metallurgist, Research Bureau, Aluminum Company of America.
† Consulting Metallurgist, Aluminum Company of America.

Composition and Properties of Duralumin

The essential elements added to commercial aluminum to produce duralumin are copper and magnesium; manganese also is generally added. The following is a typical composition: Copper 4.0 per cent., magnesium 0.5 per cent., manganese 0.5 per cent., aluminum (commercial) balance. Iron and silicon are present in commercial aluminum as impurities, so the alloy may be expected to contain about 0.5 per cent. iron and 0.3 per cent. silicon.

Duralumin, in the annealed condition, has a tensile strength of about 30,000 lb. per sq. in., an elongation of about 17 per cent., and a Brinell hardness (500-kg., 10-mm. ball) of about 50. On heating to 500° C. and quenching in water, the strength is increased to around 45,000 lb. per sq. in.; the elongation is usually also increased, say to about 21 per cent. These are the properties immediately after quenching; on standing or "aging" a spontaneous hardening takes place, ordinarily reaching substantial completion within about four days. By the end of this time the tensile strength has reached about 60,000 lb. per sq. in. and the Brinell hardness about 100; the elongation is not markedly affected.

The plasticity of the alloy is at a maximum in the annealed condition, being decreased by the quenching treatment, and still further by the aging process. This decrease in plasticity may be accompanied by an increase in elongation.

Properties of Aluminum-copper Alloys

The binary aluminum-copper alloys, free from magnesium, are affected in a manner similar to duralumin by quenching from around 500° C., but do not, to any important extent, exhibit the spontaneous hardening effect on standing at ordinary temperatures. The development of one of the new types of alloy about to be described was based on the discovery that the binary aluminum-copper alloys can be further hardened after the quenching treatment by reheating to temperatures of 100 to 200° C. and that, by the proper selection of temperature and time and composition unexpectedly high physical properties can be obtained.

Some of the early results were obtained on an alloy containing 3.95 per cent. copper, 0.35 per cent. iron, and 0.21 per cent. silicon. After quenching in water from 540° C. and aging for ten days at room temperature, the tensile strength was, in round numbers, 39,000 lb. per sq. in. and the elongation in 2 in. was 30 per cent. The same material reheated for 48 hr. at about 150° C. gave a tensile strength of approximately 48,000 lb. per sq. in. with an elongation of about 20 per cent. The reheating at 150° C., or "artificial aging," as it has been called, has thus produced an increase in tensile strength of about 23 per cent.

It was also found that the binary aluminum-copper alloys are much more easily worked than the alloys of the duralumin type containing copper and magnesium. The fact that a tensile strength of about 50,000 lb. per sq. in., coupled with a high elongation, could be obtained in a simple aluminum-copper alloy was unsuspected, and at once suggested the possibility of developing an alloy of this type that would after suitable heat treatment give physical properties similar to those of duralumin, namely, a tensile strength of about 60,000 lb. per sq. in. with an elongation of about 20 per cent., combined with improved working qualities. This has been done, and the tensile properties of the resulting alloy, after complete heat treatment, compare rather closely with those of duralumin.

The alloy now in commercial production may contain, besides copper, additions of other elements, such as manganese and silicon. It is distinguished from duralumin, chemically, by the absence of magnesium and, physically, by the fact that it does not harden spontaneously at room temperature after quenching.

While the addition of manganese, silicon, etc. are important improvements, the heat-treating effects depend primarily on the presence of copper, and can best be considered with reference to the binary aluminum-copper alloys.

Constitution of Aluminum-copper Alloys

Aluminum and copper form a hard, brittle, crystalline compound whose composition is represented by the formula $CuAl_2$, corresponding to 54 per cent. copper. This compound forms a eutectic with aluminum containing about 33 per cent. copper and melting at 548° C.[1] Copper dissolves in solid aluminum up to about 5.5 per cent. at the eutectic temperature. The solubility decreases with falling temperature, to perhaps 1.0 per cent. at room temperature.

The constitution of the alloys containing up to 8 per cent. copper is shown graphically in Fig. 1. The line AD is the liquidus, above which all alloys are completely molten. The line AB marks the end of solidification of the solid-solution alloys, and BF is the eutectic horizontal. The line BS is the solubility curve of $CuAl_2$ in solid aluminum. The phases that are stable within each region of temperature and composition are indicated in the diagram.

Theory of Heat Treatment

The idea that the variation in the solubility of $CuAl_2$ in aluminum with temperature is responsible for the heat-treating and aging effects in duralumin was first advanced by Merica[2] and his associates.

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[1] Temperature determined by C. S. Taylor, Research Bureau, Aluminum Company of America.

[2] P. D. Merica, R. G. Waltenberg, and H. Scott: Heat Treatment of Duralumin. *Trans.* (1920) **64**, 43.

They held that the effect of the quenching from around 500° C. was to bring into solid solution some of the structurally free $CuAl_2$ of the annealed metal. Suppose that an alloy containing 4.0 per cent. copper is annealed at about 350° C. and cooled slowly, and suppose that the solubility of copper in aluminum at room temperature is 1.0 per cent.; then in the annealed metal there should be 1.0 per cent. of copper in solid solution and 3.0 per cent. of copper in the form of free $CuAl_2$. Now, if the alloy is heated to a little over 500° C. and held for a sufficient time,

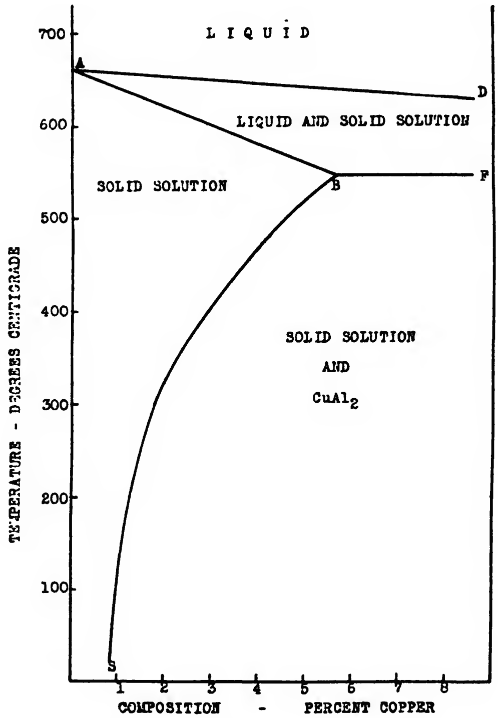

Fig. 1.—Constitution of aluminum-copper alloys.

all of the copper will be taken into solid solution. It is assumed that this solid solution is retained at room temperature by quenching. This solid solution is harder and stronger, but less plastic than the aggregate of more dilute solid solution (1.0 per cent. copper) containing relatively large particles of free $CuAl_2$.

The supersaturated solid solution retained at room temperature by quenching is unstable, and it is supposed that on standing, or aging, there is a gradual precipitation of $CuAl_2$ in the form of very fine particles. Merica postulated that the formation of this finely dispersed $CuAl_2$ is the cause of the age-hardening of duralumin.

The idea that precipitation of a compound from solid solution could cause an increase in hardness was contrary to general opinion at the time. Merica recognized that the growth of the small particles, as by annealing, caused softening. He therefore considered that there was a critical size of particle which produced maximum hardness and referred to this condition as "critical dispersion."

This theory was bold in conception inasmuch as the particles precipitated during aging are too small to be visible under the microscope and, according to Merica, remain submicroscopic even after the alloy is heated to 300° C. The evidence on which the theory is based is indirect, but strong, and subsequent work indicates that Merica's explanation is correct in principle, although it seems that in the case of duralumin another compound, Mg_2Si, is involved. It has been shown by the National Physical Laboratory, Teddington, England, that the solubility of this compound in solid aluminum decreases with decreasing temperature very much as does that of $CuAl_2$. The binary alloys of aluminum with the compound Mg_2Si show age-hardening at room temperature whereas the binary aluminum-copper alloys do not, to any substantial extent. It is a question whether the room temperature aging of duralumin is due entirely to the precipitation of Mg_2Si, or whether the presence of magnesium in the alloy induces a precipitation of $CuAl_2$ or perhaps some complex compound, at room temperature.

In the case of the binary aluminum-copper alloys, it is only the compound $CuAl_2$ that is involved. Precipitation does not occur spontaneously at room temperature, but only on heating to somewhat elevated temperatures. Effective temperatures at which to produce hardening by precipitation or aging are from 100° to 175° C.

Mechanism of Hardening

A mechanism has been[3] proposed to account for the hardening of alloys by the precipitation of a hard constituent in finely divided form. The small particles of a hard and inherently strong constituent are considered to act as "keys" on the crystallographic planes of easy slip of the matrix, mechanically opposing or "interfering" with the relative movement of crystal fragments along these planes. The effectiveness of these particles in opposing slip increases as their size decreases, because more planes can be keyed and at more points, by a large number of small particles than by a small number of large particles. The average particle diameter at critical dispersion is considered to be on the order of 10^{-7} cm.

The Aluminum-magnesium-silicon Alloys

It was shown by Wilm that alloys made by the addition of magnesium to commercial aluminum could be hardened by quenching from around

[3] Zay Jeffries and R. S. Archer: Slip Interference Theory of the Hardening of Metals. *Chem. & Met. Eng.* (1921) **24**, 1057.

500° C. followed by aging at room temperature, although Wilm seems to have been unaware, even as late as 1919, of the role of silicon in these alloys. The work at the National Physical Laboratory, mentioned above, indicated very strongly that it was the compound Mg_2Si which is responsible for the age-hardening effect.

Aluminum forms, with the compound Mg_2Si, a binary system whose constitution is represented in the diagram of Fig. 2. The maximum solubility of the compound in solid aluminum, occurring at 590° C., is 1.6 per cent., corresponding to a magnesium content of about 1.0 per cent. and a silicon content of about 0.6 per cent. This solubility decreases with temperature, like that of $CuAl_2$.

After experimenting with alloys of various compositions at the National Physical Laboratory, it was concluded that the age-hardening

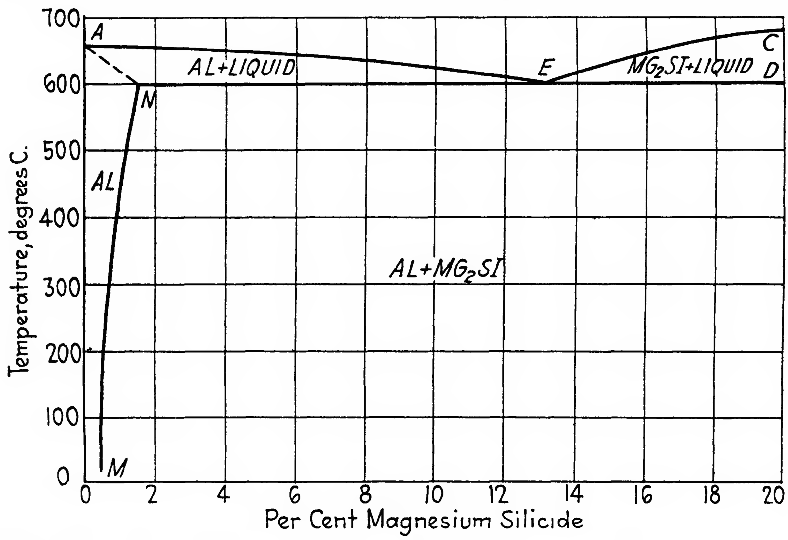

FIG. 2.—CONSTITUTION OF ALUMINUM-MAGNESIUM-SILICIDE ALLOYS, ACCORDING TO HANSON AND GAYLER.

effect was proportional to the amount of the compound Mg_2Si dissolved. The age hardening is presumably due to the formation of very small highly dispersed particles of Mg_2Si.

Consider an alloy containing 1.0 per cent. magnesium and 0.6 per cent. silicon. In the annealed condition some of the silicon and magnesium is in solid solution in the aluminum, corresponding to the solubility at room temperature. The remainder is present in the form of undissolved particles of Mg_2Si of fairly large size, say from 10^{-4} to 10^{-5} cm. in diameter. The alloy is then in its softest and most plastic state. By heating at a temperature just under the melting point of the eutectic, say 575° C., most of the Mg_2Si is dissolved in the aluminum and the solid solution is retained by quenching. This solid solution is found

to be decidedly stronger, harder, and less plastic than the aggregate from which it was formed. On aging there occurs a precipitation of Mg_2Si from this supersaturated solid solution, in the form of very fine particles; this precipitation causes a further increase in hardness and decrease in plasticity.

The strength attained in alloys of this type by quenching from a high temperature and aging at ordinary temperature is not very great—usually well under 40,000 lb. per sq. in. The Brinell hardness is only about 70, which is not enough for satisfactory machineability, nor in many cases for satisfactory resistance to deformation. The yield point is also comparatively low.

In the laboratories of the Aluminum Company of America, it was found that the hardness, strength, and elastic ratio of these alloys could be further increased to a marked extent by artificial aging, that is by heating for suitable periods of time at temperatures from about 100° to 175° C. By this means, it was possible to obtain a tensile strength as high as 54,000 lb. per sq. in., a Brinell hardness of 120, and a yield point of about 40,000 lb. per sq. in. These changes were, of course, accompanied by a decided decrease in plasticity.

This discovery greatly increased the potential usefulness of this type of alloy. It was also found that these alloys possess excellent working qualities, the capacity for cold working in particular being quite remarkable. This may be judged from the fact that, in the annealed condition, the tensile strength may be as low as 15,000 lb. per sq. in. and the Brinell hardness less than 30, values only slightly higher than those for commercially pure aluminum. A hardness increase from 28 to 120 by heat treatment alone is, we believe, of a magnitude unique among nonferrous alloys.

Two New Types of Alloy

There are thus available two new types of strong aluminum alloy, the characteristics of which may be briefly summarized as follows:

1. The aluminum-copper type: shows substantially no hardness increase on aging at ordinary temperatures after quenching from around 500° C., but is susceptible to marked hardening by reheating at 100° to 175° C. (artificial aging).

2. The aluminum-magnesium-silicon type: hardens to some extent on aging at ordinary temperatures, but is hardened to a further, and practically very important, extent by artificial aging.

Both of these types possess decidedly better working qualities than duralumin. The combination of copper and magnesium in aluminum seems to lead to comparatively poor working qualities, as in alloys of the duralumin type.

Summary of Hardening Theory

The mechanism of the changes brought about by heat treatment and aging is essentially the same for all the strong aluminum alloys. The hardening effects on aging are caused by the precipitation of hard constituents in the form of very small particles; this may take place spontaneously at room temperature or may require slightly elevated temperatures. The precipitation is from supersaturated solid solutions, formed by rapidly cooling the alloys from temperatures at which the constituents are considerably more soluble than at the aging temperature. Age hardening, therefore, depends on the presence of hard constituents, the solubility of which increases with temperature. Obviously the amount of such constituents in the alloy must exceed their solubility at the aging temperature.

Condition of Alloys after Working

The change of solubility of $CuAl_2$ and Mg_2Si with temperature seems to be most rapid just below the eutectic temperatures; as the temperature decreases, the rate of change decreases.

Most hot-working operations end at temperatures around 350° C. or lower, and are ordinarily followed by fairly slow cooling; precipitation is therefore substantially complete, and in the form of large particles. It is in this form that the hard constituents have the least effect on the strength and hardness of the alloys. When the finishing temperature after hot working is low, or when there is subsequent cold working, the alloys are "strain hardened" just as all metals are hardened by mechanical working below their temperatures of recrystallization. Such hardening is accompanied by marked decrease in ductility.

The structure of the strong aluminum alloys after the usual working is therefore favorable to softness, as regards the condition of the alloyed constituents, but this structure as a whole is hardened and embrittled to varying extents by the varying degrees of cold work that have been carried out.

Annealing

These alloys can be softened by annealing at 300° to 350° C. The removal of the hardness caused by cold working is due to recrystallization and grain growth in the aluminum-rich solid-solution matrix. Softening by this mechanism continues as the temperature is raised, and would be more effective at temperatures just under the melting point than at the intermediate temperatures given above. If annealing at such high temperatures is attempted, however, it must be followed by very slow cooling, or hardening effects will be obtained. All of these alloys are to some extent "air hardening."

The hardness of the heat-treated alloys is due to the retention of solid solution and the precipitation of many very small hard particles. These hardening causes are removed on annealing by precipitation and the growth of the precipitated particles to relatively large size.

Softening takes place slowly at temperatures as low as 150° C.; it is practically complete at 300 to 350° C.

Solution Heat Treatment

Close temperature control is required to get the best results from the solution heat treatment, for the temperature must be high enough to dissolve as much as possible of the soluble constituents but not high enough to cause any fusion. There is no sharp "critical point" that must be exceeded as in carbon steel. The process is more analogous to the hardening of high-speed steel, the degree of improvement increasing continuously with the temperature of treatment up to the point of incipient fusion. This would, of course, not be true in "mild" alloys in which the quantities of soluble constituents present became completely soluble at lower temperatures.

The time required for the solution and diffusion of the soluble constituents depends on the amount of working the material has received. In one series of experiments, it was found that for ⅛-in. sheet a heating of 2 min. gave results substantially as good as any longer period; 30 min. at heat should be sufficient for any material that has been thoroughly worked.

There is probably a critical rate of cooling from the solution treatment that will just retain the solid-solution structure, slower rates allowing more or less precipitation. The critical rate probably varies with the composition of the alloy, the temperature of the solution treatment, and to some extent with the time at heat. No attempt has been made to determine these critical cooling velocities with precision. Experiments of a qualitative nature have shown that cooling in still air is too slow. Quenching in oil seems, in some cases, to give results slightly inferior to quenching in water. Quenching in boiling water is generally held to give a sufficiently rapid rate of cooling. While cooling in still air is too slow for proper execution of the solution treatment, it is too rapid for softening.

Precipitation Treatment

The solid solutions resulting from the solution treatment are unstable at ordinary temperatures. There is a tendency for precipitation to take place. This tendency is opposed by the rigidity of the structure. The aging of duralumin that occurs naturally at room temperature is reported to be completely inhibited at the temperature of liquid air. The precipitation of $CuAl_2$ in the binary aluminum-copper alloys of

ordinary purity is practically inhibited at room temperature. These alloys must be heated above room temperature to allow the precipitation to take place freely.

The rate of precipitation increases with the temperature; precipitation can be obtained in a very short time at 250° C., for example. It is not feasible to carry out the precipitation treatment for the maximum strength at such temperatures, however, because the precipitation of the hard particles is quickly followed by particle growth with consequent softening.

This softening follows the initial hardening even at 125° C. For the commercial alloy of the aluminum-copper type, softening does not begin until after about twenty days at 125° C. At 150° C. the strength increases up to about two days and then begins to decrease. The alloy may be heated for sixty days at 125° C. or for fifteen days at 150° C., however, and still retain a strength in excess of 55,000 lb. per sq. in.

The precipitation treatment for hardening thus merges into annealing as the temperature is raised and the time extended. The regular sequence of changes during precipitation treatments at 100° to 200° C. consists of a gradual increase in strength and hardness up to a maximum, followed by a gradual decrease. The maximum is attained more quickly as the temperature is increased, but is in general higher as the temperature is decreased. The maximum in hardness may be attained after the maximum in tensile strength.

The plasticity of the alloys decreases during the precipitation treatment, at least until softening begins. In the aluminum-magnesium-silicon alloys, the elongation decreases from the beginning and continues to decrease until the point of maximum hardness is passed. The elongation of the aluminum-copper type of alloy is not greatly affected during the early stages of the treatment, especially at temperatures up to 125° C.; there may even be a slight increase in elongation. Maximum hardness, however, is accompanied by decreased elongation.

It will be apparent that the precipitation treatment may be varied both as to time and temperature according to the properties desired in the final product. If a high degree of hardness is wanted, and ductility is not important, the material may be aged at 150° to 175° C. until maximum hardness is attained. If ductility is an important consideration, it is better to carry out the treatment at 100° to 150° C. and stop before the attainment of maximum hardness.

Commercial Alloy of Aluminum-copper Type

In selecting a specific composition for a commercial alloy of this type, the aim was to provide a material having, in the fully heat-treated condition, physical properties approximately equal to those of duralumin,

but retaining the superior fabricating qualities of the aluminum-copper type.

In the final product the copper may exist in three forms: (1) In solid solution or atomic dispersion; (2) as fine, highly dispersed particles of $CuAl_2$, produced by precipitation from the solid solution at temperatures below 200° C.; (3) as relatively large particles of $CuAl_2$ that have never been in solid solution.

In any of these forms copper is a hardening agent, being most effective in the second form, then in the first form, and least effective in the third form. The hardness of the alloys may, therefore, be expected to increase with the copper content, but less rapidly after the limit of maximum solid solubility is exceeded. The homogeneity of the final product will be greater if the copper content is such that all of the $CuAl_2$ can be dissolved in the solution heat treatment. Furthermore, although large undissolved particles of $CuAl_2$ contribute to hardness, they do not necessarily contribute to strength, as they seriously interrupt the continuity of the matrix and detract from plasticity and ductility.

These considerations indicate that the maximum strength should be obtained with a copper content near the limit of solid solubility, which appears to be about 5.5 per cent. Practically, however, it is impossible to take full advantage of this maximum solid solubility on account of the very close temperature control that would be required. This maximum solubility occurs only at the eutectic temperature. A solution heat treatment carried out a few degrees below this temperature would fail to result in complete solution, and a treatment a few degrees above the eutectic temperature would cause incipient fusion and ruin the material.

Copper in any of the forms described decreases the plasticity of the alloys (although not necessarily the per cent. elongation in the tensile test). The alloys are, therefore, more workable, the lower the copper content. The selection of copper content thus becomes a compromise between strength and workability, with the maximum amount indicated at about 5.5 per cent., unless for some special purpose greater hardness is desired.

Silicon also has been found useful as a strengthening addition. The function of silicon is complicated by its apparent interaction with the iron present as an impurity. It has been found that the addition of iron alone, in sufficient amount, greatly decreases the strength of the alloys and even seems to inhibit the improvement by heat treatment. An alloy containing 3.94 per cent. copper, 1.22 per cent. iron, and 0.31 per cent. silicon, tested in the form of ⅛-in. sheet, had a tensile strength of only 31,450 lb. per sq. in. after quenching from 530° C. and aging five days at room temperature. On aging for 22 hr. at 150° C., the strength was not increased. This quantity of iron would not ordinarily be encountered in alloys made from a good grade of aluminum ingot, but the example

illustrates the direction of the effect of iron. Silicon seems to be able to counteract, to some extent, the effect of iron, probably by the formation of an iron silicide or a ternary compound containing aluminum, iron, and silicon. In addition to its interaction with iron, silicon may exert a strengthening effect by entering the solid solution, for it is appreciably soluble in solid aluminum.

The harmful effect of iron on the strength of these alloys and the possibility of partly neutralizing this effect by the addition of silicon are illustrated by the following examples: An alloy was made up containing approximately 3.75 per cent. copper with the usual amount of silicon, but with an iron addition of about 1 per cent. An ingot was cast from this alloy and an addition was then made of about 1 per cent. silicon. A second ingot was then cast. Both ingots were forged in the same manner and specimens were heat treated together. The analyses of the two lots of material were as follows:

No.	Copper, Per Cent.	Iron, Per Cent.	Silicon, Per Cent.
3507	3.76	1.22	0.22
3508	3.58	1.17	1.16

Immediately after quenching in water from 528° C., the tensile properties of these alloys were as follows:

No.	Tensile Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.
3507	28,090	29.5
3508	38,750	29.25

Specimens given an additional treatment of 18 hr. at 150° C. had the following properties:

No.	Tensile Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.
3507	27,735	31.0
3508	42,595	23.25

Manganese has been found to increase the strength of the alloys and to impart a somewhat fibrous structure, which seems to favor the retention of ductility when the precipitation process is carried towards completion. A suitable manganese content is 0.5 to 1.0 per cent.

Commercial Alloy of Aluminum-magnesium-silicon Type

This type of alloy can be made surprisingly soft by annealing, its hardness in the softest condition comparing with that of ordinary "pure" aluminum. Combined with this is a great potential hardening power. The Brinell hardness can be quadrupled by a suitable combination of composition and heat treatment. The tensile strength attainable is only about 54,000 lb. per sq. in. and even this is at a considerable sacrifice of ductility. As the aluminum-copper alloy provides higher strength when necessary, it seems advisable in the aluminum-magnesium-silicon

type of alloy to take full advantage of the remarkable cold-forming properties rather than strive for the maximum strength and hardness.

Theoretically, maximum hardening power should be obtained when the ratio of silicon to magnesium is just right to form the compound Mg_2Si. Actually, the iron content of the alloy must be taken into account, as the iron may combine with some of the silicon and render it insoluble. It is, therefore, logical that the silicon content should exceed the theoretical ratio. The amounts of magnesium and silicon to be used are governed somewhat by the principles described in connection with the aluminum-copper alloys. It has been found, however, that when the amount of Mg_2Si present is considerably less than that required to form a saturated solid solution, an addition of an excess of either magnesium or silicon materially increases the hardness and strength. This may be due to their effects *per se* or to their effects on the solubility of Mg_2Si.

Mechanical Properties

The development of the full mechanical properties of which the alloys are capable is dependent on thorough mechanical working. These alloys are available in the form of sheet, bar, rod and wire, tubing, and shapes both rolled and extruded. Sheet in thicknesses up to ⅛ in., wire and bar up to ¾-in. diameter, tubing and extruded molding and shapes may be considered as worked sufficiently to insure the development of the maximum properties. This applies to present average commercial practice. When necessary, comparable degrees of mechanical working may be obtained in heavier sections by starting with larger ingots. This has been done in the case of some heavy forgings.

Cold Worked

These alloys are ordinarily used only in the heat-treated condition. It may, nevertheless, be of interest to indicate the properties that may be expected as the result of hot working followed by more or less cold working. After such treatment the aluminum-copper alloy will, in general, have a tensile strength of 30,000 to 45,000 lb. per sq. in. with an elongation of 10 to 3 per cent. in 2 in.; while the aluminum-magnesium-silicon alloy will have a tensile strength of about 17,000 to 30,000 lb. per sq. in. with an elongation of 15 to 5 per cent.

As Extruded

Extruded material receives a partial heat treatment from its method of manufacture and, consequently, has a fair tensile strength combined with a very good elongation, as compared with cold-worked material. The following are typical values, although considerable variations are to be expected on account of variations in the conditions of extrusion.

Alloy	Tensile Strength, Lb. per Sq. In.	Yield Point, Per Cent.	Elongation in 2 In., Per Cent.	Brinell Hardness, 10-mm. Ball, 500-kg.
Al-Cu	30,000–40,000	15,000–20,000	10–18	50–65
Al-Mg-Si	20.000–30.000	9.000–13.000	18–25	40–55

Annealed

After annealing at about 350° C., followed preferably by slow cooling, these properties may be expected:

Alloy	Tensile Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.	Brinell Hardness, 10-mm. Ball, 500-kg.
Al-Cu	25,000–35,000	15–20	45–55
Al-Mg-Si	14,000–18,000	15–30	23–30

As Quenched

The range of temperature recommended for the solution treatment is 515° to 540° C., which is suitable for both alloys. After quenching from this temperature, it will be remembered, the aluminum-copper alloy is substantially stable at ordinary temperatures whereas the aluminum-magnesium-silicon alloy undergoes a certain amount of age-hardening. The properties here given include the effect of this room temperature or "natural" aging.

Alloy	Tensile Strength, Lb. per Sq. In.	Yield Point, Lb. per Sq. In.	Elongation in 2 In., Per Cent.	Brinell Hardness, 10-mm. Ball, 500-kg.
Al-Cu	45,000–53,000	18,000–25,000	15–20	70–85
Al-Mg-Si	30,000–40,000	15,000–20,000	20–30	55–70

Heat-Treated Temper

The fully heat-treated condition includes the effects of both solution and precipitation treatments. The precipitation may be varied considerably according to the properties desired. The properties here given are considered suitable for average purposes, and are generally obtained by a precipitation heat treatment of from 4 to 18 hr. at 100° to 160° C.

Alloy	Tensile Strength, Lb. Per Sq. In.	Yield Point, Lb. per Sq. In.	Elongation in 2 In., Per Cent.	Brinell Hardness 10-mm. Ball, 500-kg.
Al-Cu	55,000–63,000	30,000–40,000	18–25	90–110
Al-Mg-Si	45,000–50,000	30,000–40,000	10–18	85–100

Other Physical Properties

Young's modulus E for both alloys is about 10,000,000 lb. per sq. in.

The specific gravity of the aluminum-copper alloy is about 2.79, and of the aluminum-magnesium-silicon alloy about 2.69.

In the fully heat-treated condition, the aluminum-copper alloy has an electrical conductivity of about 30 to 35 per cent. of the annealed

copper standard, while for the aluminum-magnesium-silicon alloy the values are approximately 40 to 45 per cent.

The thermal conductivities, in C. G. S. units, are numerically very close to the above electrical conductivity values.

Machineability

These alloys in the heat-treated temper are readily susceptible to all ordinary machining operations. A somewhat novel application has consisted in machining from the aluminum-magnesium-silicon alloy, in the heat-treated condition, certain parts that are then annealed for a service that would otherwise require pure aluminum, a material quite difficult to machine.

Combination of Types

It will be apparent that duralumin is a combination of the two types of alloy here described, inasmuch as it contains copper and magnesium, both intentionally added, together with some silicon, which was present in the aluminum ingot as an impurity. The amount of silicon present in an aluminum ingot is quite variable, however, hence the amount obtained in duralumin by accident may or may not be most suitable. In view of the beneficial effects of silicon, alloys have been prepared of the duralumin type but containing more than the usual amount of silicon. A typical example of this type of alloy contained 4.32 per cent. copper, 0.78 per cent. silicon, 0.50 per cent. magnesium, and 0.49 per cent. manganese. After forging, this alloy was heated to a temperature between 500° and 515° C. and quenched in water. After aging for three days at room temperature, the tensile strength was 59,300 lb. per sq. in. and the elongation, 25 per cent. Artificial aging for 70 hr. at 120° C. raised the tensile strength to 66,900 lb. per sq. in. with an elongation of 20.5 per cent. After a precipitation heat treatment of 20 hr. at 150° C., the tensile strength was 75,300 lb. per sq. in. and the elongation, 13 per cent. Thus, by combining the new information regarding composition and heat treatment, it has been possible to produce an alloy of the duralumin type having greater strength and hardness than hitherto produced by heat treatment.

The strength of all of these aluminum alloys can be increased by cold working after heat treatment, but this added strength is obtained at a great sacrifice of elongation.

Technical Methods of Heat Treatment

The main requirement in the heat treatment of the strong aluminum alloys is accuracy of temperature control. This applies more to the solution heat treatment and the precipitation heat treatment than to annealing. The problem of securing uniform and exact temperatures is

somewhat more difficult than in the heat treatment of steel because the temperatures are all below a visible red heat. The color of the material cannot, therefore, be used as an indication of uniformity of temperature distribution. On the other hand, the heat treatment is simplified by the perfect resistance of aluminum and its alloys to air at all temperatures up to the melting point. An air atmosphere is, in fact, ideal for all of the heat treatments. The time interval between the removal of the metal from the heating bath or furnace and its quenching must be as short as possible if best results are to be obtained.

Accuracy and uniformity of temperature control, especially at low temperatures, are probably best secured by the use of liquid heating baths. It is not sufficient merely to employ a liquid bath; as considerable temperature differences may exist in a still body of liquid, it is necessary to circulate the bath thoroughly. For the solution heat treatment, it is quite common to use a bath of molten salt such as sodium nitrate. This bath is contained usually in a steel tank. Aluminum-alloy articles can be heated rapidly by immersion in such a bath. It is then common to quench them in hot water, to facilitate the removal of the adhering salt. If the aluminum is allowed to cool slowly, the salt forms a sort of enamel that is very difficult to remove. In any event, the salt must be completely removed as it may otherwise cause corrosion later on.

For the precipitation heat treatment, a bath of circulating oil may be used as in the tempering of steel. This is an ideal method of securing quick heating and close temperature control. Of course, it involves the disadvantage of leaving the articles covered with oil.

In spite of the desirable thermal properties of salt baths for the solution heat treatment, the method is somewhat expensive and also somewhat objectionable because of the possibility of stimulating corrosion. A salt bath would be especially expensive for the heat treatment of massive articles, such as forgings, so its use is, in general, restricted to light articles, such as sheet and tubing. For forgings and bars, it is common to use electrically heated furnaces with automatic temperature control. With proper furnace design and proper disposition of the work, satisfactory uniformity of temperature distribution can be obtained. The heating is much less rapid in this case so a longer time must be allowed in the furnace. Heating periods as long as 24 hr. have been used for heavy charges. It is not advisable to allow the maximum furnace temperature to exceed the upper limit of the heat-treating range, therefore the rate at which the work comes up to heat is quite slow toward the end of the heating cycle.

Very good temperature control and distribution can be obtained for the precipitation heat treatment by the use of live steam, as in tanks employed for vulcanizing. This method insures rapid heating and the temperature can be accurately controlled by a pressure-regulating device.

The steam has some action on the surface of the aluminum, especially if the solution heat treatment has been carried out in niter. This surface action is more serious with thin than with heavy material. It is fairly objectionable in the case of sheets, for example, and not of much consequence in the case of forgings. The pressures needed to obtain the usual temperatures for the precipitation process will not, as a rule, exceed about 75 lb. in the line. This method is usually economical only when there is a source of steam available at all hours for other purposes.

The precipitation heat treatment may be carried out in an air atmosphere in an oven of the type used for enamelling or core baking, provided the temperature control and distribution are satisfactory. Such ovens may be heated electrically or by steam coils or by coils through which hot oil is circulated.

Annealing is generally carried out in an air atmosphere. The salt bath would be ideal because rapid heating is desirable but it would be difficult to remove the salt if the metal were cooled slowly and it is undesirable to quench the metal because of the danger of hardening if the temperature should be too high and because of the distortion produced by the quenching operation.

Considerable distortion may result from the solution heat treatment. This distortion may be caused in three ways:

1. During the heating of the metal when it is quite soft and subject to distortion by its own weight or by the weight of objects lying on it.

2. In the operation of transferring the metal from the furnace to the quenching bath, the metal is soft and precautions must be taken to avoid distortion in handling.

3. The operation of quenching sets up stresses, which may result in distortion. These stresses are less the slower the rate of cooling. Boiling water, for example, produces less stress than cold water, and air cooling less than either.

Applications

The alloys here described are, in general, applicable where it is desired to obtain high tensile strength and ductility combined with the lightness, corrosion resistance, and other desirable qualities of aluminum. The alloy of the aluminum-copper type is suitable for the same applications as duralumin and has the advantage of distinctly better fabricating qualities. The alloy of the aluminum-magnesium-silicon type is strong enough and hard enough for many purposes for which duralumin might otherwise be used and is remarkable for ease of forming.

The alloy of the aluminum-copper type is being used in the form of forgings for highly stressed parts such as automobile connecting rods and aircraft propellers. The alloy of the aluminum-magnesium-silicon

type is very suitable for a great variety of hardware in which considerable strength and hardness are desired but in which the strength of the aluminum-copper alloy is not necessary.

Where very severe cold-forming operations are to be performed, the alloy of the aluminum-magnesium-silicon type can be used where none of the other strong alloys will stand the operations.

DISCUSSION

F. B. Coyle, Brooklyn, N. Y.—In the Navy we are interested chiefly in the resistance to salt-water corrosion. We have made many parts from aluminum for some of the submarines—deck plates, hatch covers and some very large castings. Would the addition of a small percentage of magnesium aid in the aluminum-silicon alloys?

M. F. Fogler,* Chicago, Ill.—We have been interested in some work with alloys of a similar nature to that just discussed. The authors say that immediately after quenching, these aluminum alloys show an increase in tensile strength and hardness. The system we are working with, immediately after quenching, shows no greater Brinell number or tensile strength than after the annealing period. The increase in hardness in the first few days is very rapid, after that it is slow; it takes two weeks or so to reach its maximum, after which there is a gradual falling off.

In connection with rolling, the authors stated that by rolling either before or after the heat treatment they were able to increase the tensile strength and hardness of these aluminum alloys. If we roll this alloy immediately after quenching nothing happens; there is no increase in hardness. The alloy cannot be rolled after it hardens.

Conductivity measurements on this alloy before and after heat treatment show that after heat treatment the conductivity is much lower, then it gradually increases on aging. In view of the effect of the separation of the particles, thus giving a mixture rather than a solid solution, from the ordinary ideas of conductivity, one would expect an increase in conductivity. I think this supports, in some measure, the idea of the separation of the solute in colloidal form.

H. S. Rawdon, Washington, D. C.—What is the function of the manganese?

Zay Jeffries.—Magnesium added to the aluminum silicon casting alloys increases the yield point. Manganese, in the duralumin-type alloys, acts mainly to harden the matrix, if we consider the aluminum solid solution as the matrix of the duralumin alloy. The total hardness and strength will be a function of the hardness of the matrix plus the

* Metallurgical Engineer, Western Electric Co.

increase in hardness in that matrix due to the precipitation of the $CuAl_2$ or Mg_2Si. Manganese increases the tensile strength of the alloy in the quenched condition about as much as it does the strength of the final alloy; therefore, the hardening due to the aging effect or to the precipitation is added to the hardness of whatever matrix one has to begin with. So starting with the aluminum matrix, strengthening that matrix with the addition of manganese, then perhaps still further strengthening it by the addition of silicon, gives a matrix that is already quite hard and strong, and the added hardness and strength caused by the precipitation gives the final result, which is materially better than that which can be obtained without the manganese or the silicon.

D. J. McAdam, Jr.,* Annapolis, Md. (written discussion).†—The authors have done valuable work in investigating and distinguishing between the two types of alloy that exist in duralumin. They have developed details of heat treatment and have studied the effect of time and temperature in first hardening and then softening the alloys.

Rosenhain, Archbutt, and Hanson, in the Eleventh Report to the Alloys Research Committee of the Institution of Mechanical Engineers (August, 1921) discuss in great detail the aluminum-copper alloys and the aluminum-magnesium-silicon alloys. They discuss the age hardening of aluminum-magnesium-silicon alloys at ordinary temperature and present graphs showing the effect of aging for one hour at temperature up to 400° C. The temperature at which maximum hardness is produced under these conditions is about 200° C. and the increase in hardness, of alloys containing magnesium and silicon in nearly the proportions of the compound Mg_2Si, is about 50 per cent. Increase in annealing temperature above about 200° C. causes softening.

The Eleventh Report also discusses the aging of aluminum-copper alloys containing 0.5 to 5.0 per cent. copper. The authors of this report present data indicating that an aging effect at room temperature is apparent in all alloys containing 2.5 to 5.0 per cent. copper, but the actual increase in hardness is only small. They say that this is quite insufficient by itself to account for the hardening effect produced in duralumin. They then reheated the alloys to successively higher temperatures for one hour and found that a maximum hardening effect was produced by a temperature of about 200° C. By this treatment the maximum increase in hardness of the 4 per cent. copper alloy above that obtainable by aging at room temperature was about 50 per cent. Annealing at a temperature above about 200° C. caused softening.

The British authors do not agree with American investigators in regard to the solubility of $CuAl_2$ at room temperature. They assert

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† Printed by permission of the Secretary of the Navy.

that the saturated alpha solution at room temperature contains about 3 per cent. copper instead of about 1 per cent. as indicated by investigation in this country.

The authors of the present paper deserve credit for investigating the practical possibilities of age hardening at elevated temperatures somewhat lower than those used by the British investigators. With the lower temperature and increased time of annealing, it is possible to stop the process accurately at the point of maximum hardness and thus probably obtain better physical properties than those possible with the treatment for one hour at 200° C.

The authors have pointed out that the aluminum-copper alloy and the aluminum-magnesium-silicon alloy have better working qualities than duralumin. They do not mention the endurance properties of these alloys. It will be of great interest to know if either of these new alloys has better endurance properties than duralumin. Duralumin was a great disappointment in this respect. Although it has the tensile strength of mild steel, its endurance limit is less than half that of mild steel.

Endurance Properties of Duralumin

The endurance properties of duralumin, as determined at the Naval Engineering Experiment Station, are illustrated in Fig. 3. The small circles represent results of individual endurance tests obtained with quenched and aged duralumin. The zigzag line ending in the center of a circle represents the course of an endurance test in which the initial

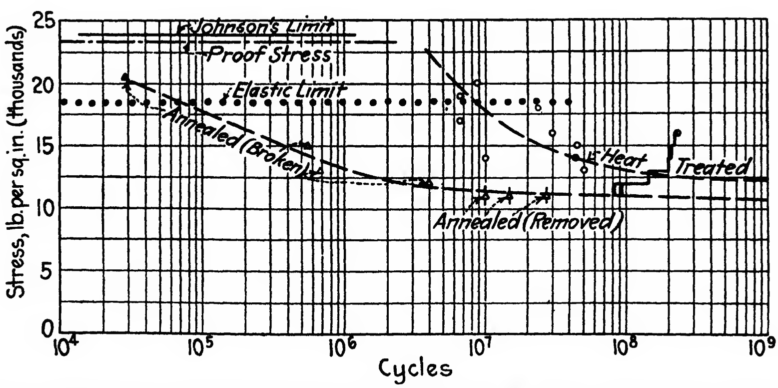

Fig. 3.—Results of endurance test on duralumin by rotating-cantilever method.

alternating stress of 11,000 lb. per sq. in. was maintained for about 80,000,000 cycles, then raised to 12,000 lb. and maintained for 70,000,000 cycles, then raised to 13,000 lb. and maintained for 50,000,000 cycles. These increases of stress were continued until the specimen finally broke at a stress of 16,000 lb. per sq. in. after enduring a total of about 230,000,-

000 cycles. The triangles represent results obtained with annealed duralumin. The upper and lower broken lines represent average stress-cycle relationship for quenched and aged duralumin and for annealed duralumin respectively.

As shown, the average endurance limit for the quenched and aged duralumin with a tensile strength of 53,400 lb. is 12,000 or 13,000 lb. per sq. in. The average endurance limit for annealed duralumin with a tensile strength of 29,500 lb. is 10,000 or 11,000 lb. per sq. in. Enhancement of the tensile strength 80 per cent. by heat treatment, therefore, has not increased the endurance limit of duralumin more than 20 or 25 per cent. above that of annealed material.

Horizontal lines have been drawn, in Fig. 3, to represent the proof stress,[4] Johnson's limit, and elastic limit of the quenched and aged duralumin. The field of usefulness of this duralumin is represented by the area below the dotted line of elastic limits and below the broken line representing average stress-cycle endurance relationship. As shown by these two lines meeting at an abscissa of about 9,000,000 cycles, whether the elastic limit or the endurance properties are of greater importance depends on the number of cycles of stress that the material will undergo in service. If in service duralumin is to be subjected to less than about 9,000,000 repetitions of important stress range, the basis of design should be the elastic limit. If more than about 9,000,000 repetitions of an important stress range must be endured, the basis of design should be the endurance limit.

Specific Endurance

In order that a light alloy may compete with other metals and alloys that are used in machinery parts in which endurance properties are of chief importance, the endurance limit must be above a minimum that depends on the specific gravity.

Two cylindrical machinery parts have equal endurance for repeated tension-compression when $\frac{S'}{S} = \frac{D^2}{D'^2}$; where S represents the endurance limit and D the diameter. Under such conditions $\frac{W}{W'} = \frac{D^2G}{D'^2G'}$ in which W represents total weight and G the specific gravity. $\therefore \frac{W}{W'} = \frac{S'}{S} \cdot \frac{G}{G'}$ or $\frac{W}{W'} = \frac{\frac{S'}{G'}}{\frac{S}{G}}$. The total weights are, therefore, inversely proportional

[4] By "proof stress" is meant the stress that produces a permanent set of 0.01 per cent.

to $\frac{S}{G}$. The specific endurance for repeated tension compression may, therefore, be represented by $\frac{S}{G}$.

Two cylindrical machinery parts have equal endurance for repeated bend or torsion, when $\frac{S'}{S} = \frac{D^3}{D'^3}$. But $\frac{W}{W'} = \frac{D^2G}{D'^2G} \therefore \frac{W}{W'} = \left(\frac{S'}{S}\right)^{2/3} \frac{G}{G'}$, or $\frac{W}{W'} = \frac{S'^{2/3}}{G'} \div \frac{S^{2/3}}{G}$. The total weight is proportional to specific gravity

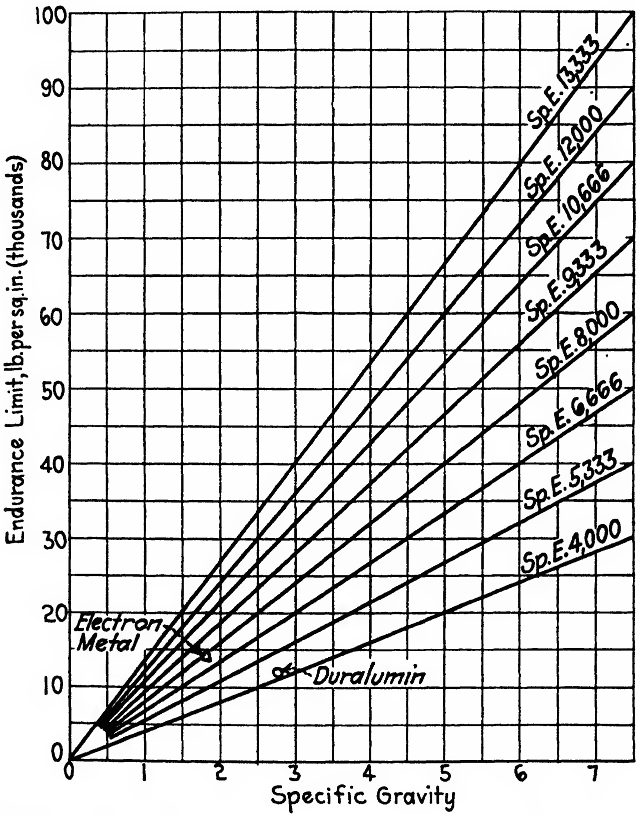

FIG. 4.—SPECIFIC ENDURANCE; REPEATED TENSION OR COMPRESSION.

and inversely proportional to the endurance limit raised to the two-thirds power. Specific endurance for repeated bending or torsion, therefore, may be represented by $\frac{S^{2/3}}{G}$.

Two alloys of equal specific endurance can compete on terms of equality for use in machinery parts in which lightness is of primary importance. As the specific-endurance formulas for tension compression

and for repeated bending or torsion are different, it is evident that two alloys which compete on equal terms for the former use do not compete on equal terms for the better use.

Fig. 4 illustrates specific-endurance relationship for repeated tension and compression. Abscissas represent specific gravity, the maximum abscissa representing the approximate specific gravity of steel. Each

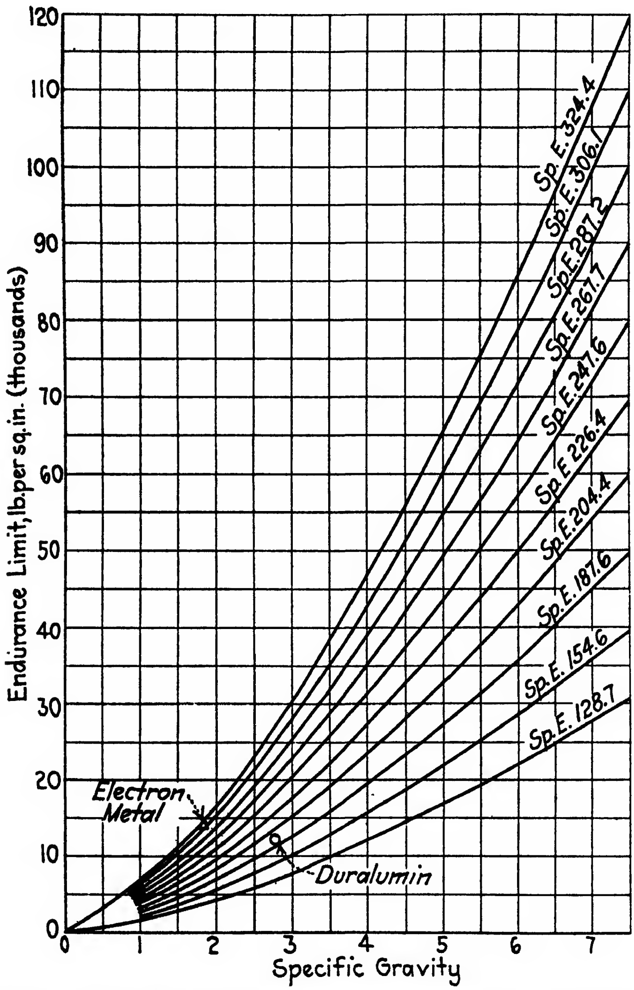

FIG. 5.—SPECIFIC ENDURANCE, REPEATED BENDING OR TORSION.

sloping line represents a series of alloys of equal specific endurance. The tangent $\frac{S}{G}$, of the angle of slope of each line represents a specific endurance number.

Fig. 5 represents specific-endurance relationship for repeated bending or torsion. As under these conditions, specific endurance $= \frac{S^{2/3}}{G}$, the lines of equal specific endurance in this figure are curved.

Two of the commercial light alloys are represented, in Figs. 4 and 5, by a small circle and a triangle. In repeated tension and compression, as shown in Fig. 4, duralumin could theoretically compete on equal terms with steel having an endurance limit of 30,000 lb. per sq. in. Such steel would be low-carbon steel having a tensile strength of about 60,000 lb. per sq. in. In repeated bending or torsion, duralumin could theoretically compete with steel having an endurance limit of about 53,000 lb. per sq. in. Such steel would be a heat-treated carbon or alloy steel. The highest grade of heat-treated alloy steels, however, which may have an endurance limit of 75,000 lb. per sq. in., far exceed duralumin in specific endurance.

Electron metal, as it is considerably lighter than duralumin and has as high endurance limit, is considerably higher in specific endurance, as shown in Figs. 4 and 5. Theoretically it could compete in repeated tension and compression with an alloy steel having an endurance limit of 60,000 lb. per sq. in., and in repeated bending or torsion with an alloy steel having an endurance limit of about 115,000 lb. per sq. in.

Practically, however, light alloys such as duralumin or electron metal would not be used to replace steel unless the replacement would reduce weight considerably. Assuming that a reduction of weight of one-third would be an incentive for the use of a light alloy to replace steel for practical competition, the light alloy must have one and one-half times the specific endurance of the steel. On this basis, duralumin could not compete in repeated tension and compression with any steel, but could compete in repeated bending or torsion with a mild steel having a specific endurance of about 130 and an endurance limit of 30,000 lb. per sq. in. Electron metal on the same basis could compete in repeated tension and compression with mild steel and in repeated bending or torsion with an alloy steel having an endurance limit of 60,000 lb. per sq. in.

As previously mentioned, the endurance limit of heat-treated duralumin is only slightly greater than that of annealed duralumin. It is possible that one or both of the new alloys described by the authors may have a higher endurance ratio than that of heat-treated duralumin. If the endurance ratio should be equal to that of electron metal, the new alloys would have endurance limits from 20,000 to 25,000 lb. per sq. in., nearly twice the endurance limit of duralumin.

The failure of heat treatment of duralumin to increase the endurance limit is not the only example of such failure. In recent papers on endurance properties of nickel and of copper,[5] evidence was presented that

[5] D. J. McAdam, Jr.: Endurance Properties of Alloys of Nickel and of Copper. *Trans.* Amer. Soc. Steel Treat. (1925) 7, Nos. 1 and 2.

increasing by heat treatment the tensile strength of copper-zinc alloys of duplex microstructure causes practically no increase in the endurance limit. Increasing the tensile strength of a metal by precipitating a hard compound or compounds from solid solution, therefore, may not prove to be an efficient method of raising the endurance limit. These papers showed that by solid solution of another metal in copper the endurance limit is increased usually more than in proportion to the increase in tensile strength. It would seem desirable, therefore, that an attempt be made to produce by solid solution an aluminum alloy having a higher endurance limit than that of duralumin. A great obstacle to the development of light alloys of high endurance is the fact that solid solutions of most of the well-known metals, such as iron, nickel and copper, in aluminum have low saturation limits. If, for example, it were possible to dissolve nickel in solid solution in aluminum up to 10 or 15 per cent., probably a light alloy of high specific endurance would be obtained. Whether any heavier metal except zinc goes into solid solution in aluminum in large proportion is not known to the writer.

In the preparation of solid solutions of other metals in aluminum for investigation of endurance properties, it would be necessary to use aluminum of higher than commercial purity. The relatively large proportions of iron and silicon in commercial aluminum would make it impossible with such material to obtain alloys containing only one microconstituent. If aluminum of purity anywhere near to that of electrolytic copper were available for experiment, it seems probable that the knowledge of aluminum alloys would rapidly increase.

A saturated solid solution of magnesium in aluminum contains 8 or 9 per cent. of magnesium. The endurance properties of this alloy should be investigated. Its specific gravity would be less than that of aluminum. Therefore, even if its endurance limit should be only equal to that of duralumin, its specific endurance would be greater.

Binary and ternary solid solutions of magnesium, copper, zinc, manganese, and other metals in aluminum should be investigated to determine the solid solutions of highest endurance limit. With such solid solutions, a further investigation could be made of the possibilities of raising the endurance limit still further by precipitating from solid solution a second microconstituent.

Horace C. Knerr,* Philadelphia, Pa. (written discussion).—The contribution of two new high-strength light alloys to the engineering materials available is of great importance to industry; especially to the engineering profession. Such materials open the way to engineering developments that otherwise would be impossible or impracticable; for example, the airship. In these applications, cost is a secondary considera-

* Metallurgical Engineer, Naval Aircraft Factory.

tion. Perhaps even more important are the savings obtainable through an intelligent substitution of light alloys for the heavy metals at present used in structural parts whose weight entails an economic loss, notably in automobiles, electric and steam railway cars, vessels, and in the reciprocating parts of engines. Hitherto, the high cost of light alloys, entailed by difficulties in their manufacture and fabrication, has prevented their extensive application in this field. If these difficulties can be avoided and the consumer given the benefit of the decreased cost, the results are likely to be far reaching.

Strength-weight Factors

The value of light alloys may, for many purposes, be compared with that of the heavier materials, on the basis of the "strength-weight" factor; that is, the tensile strength divided by the specific gravity. Some typical examples are:

	Tensile Strength		Specific Gravity		Strength-Weight Factor
Duralumin	55,000	÷	2.80	=	19.3
Aluminum-copper alloy	55,000	÷	2.80	=	19.3
Alloy steel	150,000	÷	7.85	=	19.1
Aluminum-magnesium-silicon alloy	45,000	÷	2.69	=	16.7
Steel, cold-rolled	60,000	÷	7.85	=	7.6
Brass, rolled	55,000	÷	8.4	=	6.5
Aluminum (soft)	12,000	÷	2.7	÷	4.4

It is evident that aluminum, on the basis of strength for a given weight, is a heavy material of construction, and that duralumin and the new light alloys compare with alloy steel having a tensile strength in the neighborhood of 150,000 lb. per sq. in.

Heat Treatment

The authors have referred to difficulties in the heat treatment of light alloys. After six years of experience in the use of duralumin for aircraft parts, the writer is of the opinion that its heat treatment is considerably simpler and less difficult than that for steel, especially alloy steel having a strength-weight factor as high as that of duralumin.

Air Quenching

Tests[6] have shown that very nearly, if not quite, as good tensile properties may be obtained in thin sheet duralumin by heating in an electric muffle furnace, withdrawing and allowing to cool in air, as are obtainable by quenching in water or oil. This avoids serious difficulties in the treatment of large parts, such as fuel tanks, cowling, etc. for aircraft, which would be badly distorted by quenching in a liquid bath. The method opens some new fields of usefulness.

[6] H. C. Knerr: Duralumin—A Digest of Information. *Trans.* Am. Soc, Steel Treat. (1922).

Corrosion

Corrosion resistance has also been mentioned. The writer feels that a word of caution on this point may not be out of place. Duralumin was heralded as a "corrosion-resistant material." This led many to suppose that it was immune from attack by fresh or salt water. Duralumin and aluminum corrode very little when exposed to moisture for short periods followed by drying, but direct and constant exposure for long periods, especially in salt water, causes severe corrosion with ultimate destruction of the material. Attack may be retarded or prevented by suitable protective coatings, so that duralumin has been successfully used in the hulls of flying boats. Presumably, the behavior of the new alloys would be similar.

The speed of cooling from the quenching temperature has a pronounced effect on the corrosion-resisting properties of duralumin, the slower cooling giving less resistance to corrosion. The influence of rate of cooling on corrosion is much greater than on tensile properties. Air-quenched specimens corrode much more rapidly when exposed to moisture than do specimens quenched in water, although the tensile properties do not differ greatly.[7] It would be interesting to know whether the new alloys are similarly affected.

Welding

It would also be interesting to have data on the welding properties of the new alloys, compared with those of duralumin. The latter may be welded by either the gas or electric-resistance method with excellent results. Gas welding, however, is attended by some difficulties, and special precautions to avoid shrinkage cracks are necessary.[8] If the welding of the new alloys is easier, their value will be considerably increased.

Ernest Schweizer,* New Brunswick, N. J. (written discussion). The development in aluminum alloys has been rather slow, because of the policy of various companies to keep its information a secret. The research laboratory of the Aluminum Company of America is an exception to the general rule and has contributed greatly to our knowledge of aluminum and its alloys.

The first attempts for improving the qualities of aluminum were by alloying it with other metals without subsequent heat treatment. The heat treatment of aluminum alloys began in 1903, when the D. R: P. 170085 was granted to the Central Stelle für wissenschaftliche Unter-

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* Metallurgist, International Motor Co.

[7] H. C. Knerr: *Op. cit.*

[8] H. C. Knerr: Welding Duralumin. *Auto. Ind.* (May 4, 1922).

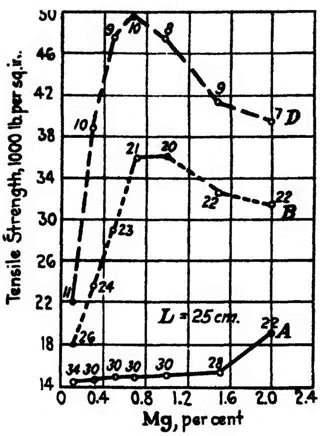

Fig. 6.

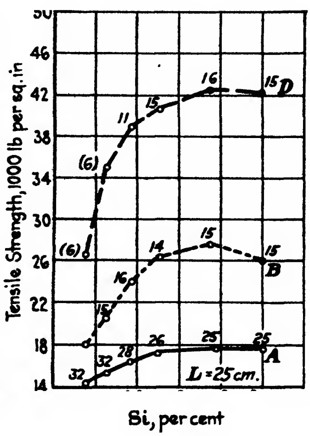

Fig. 7.

Fig. 6.—Effect of magnesium on the tensile strength of aluminum containing 0.7 per cent. silicon and approximately 0.4 per cent. iron.

Fig. 7.—Effect of silicon on the tensile strength of aluminum containing 0.3 per cent. magnesium and approximately 0.4 per cent. iron.

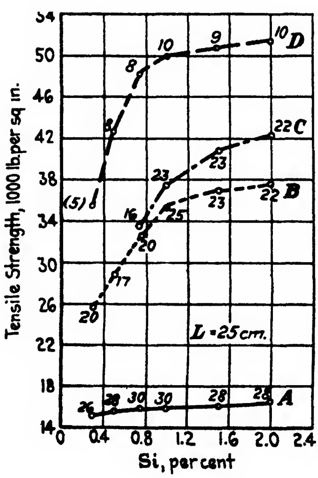

Fig. 8.

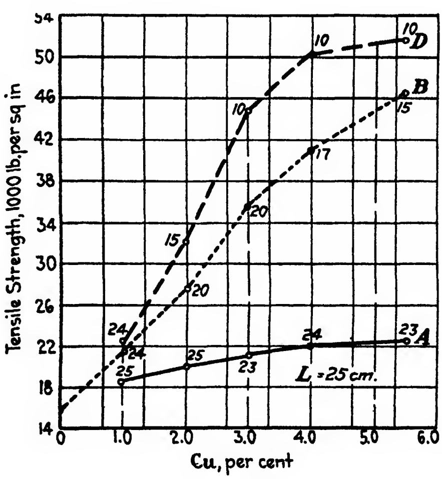

Fig. 9.

Fig. 8.—Effect of silicon on the tensile strength of aluminum containing 0.6 per cent. magnesium and approximately 0.4 per cent. iron.

Fig. 9.—Effect of copper on the tensile strength of aluminum containing approximately 0.6 per cent. silicon and 0.4 per cent. iron.

A, heated at 300° C. for 3 hr.: *B* (Figs. 6 and 8) heated at 550° C. approximately ½ hr., quenched in water and measured soon after quenching (Figs. 7 and 9 were heated at 500° C.); *C*, heat treated same as *B*, aged at room temperature for about 1 week; *D*, heat treated same as *B*, hardened at 160° C. to maximum tensile strength. Numbers plotted indicate per cent. elongation of test pieces.

suchungen G. m. b. H. Neubabelsberg covering the hardening of aluminum alloys by quenching them from a certain higher temperature to a lower one. A special example, aluminum with 4 per cent. copper, was mentioned.

The first great success was in 1909, when Wilm was granted D. R. P. 244554, showing that aluminum alloys harden at room temperatures after a treatment at certain higher temperatures. The necessity of quenching from the higher temperature was not mentioned in this patent, probably to avoid interference with D. R. P. 170085. Portevin and Arnon, in

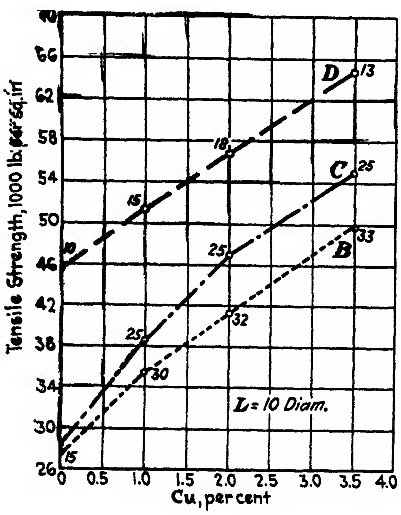

Fig. 10.

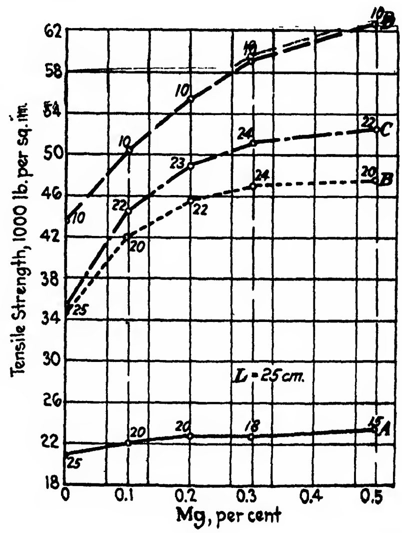

Fig. 11.

Fig. 10.—Effect of copper on the tensile strength of aluminum containing 0.5 per cent. magnesium, and approximately 0.6 per cent. silicon and 0.4 per cent. iron.

Fig. 11.—Effect of magnesium on the tensile strength of aluminum containing 3 per cent. copper and approximately 0.6 per cent. silicon and 0.4 per cent. iron.

A, heated at 300° C. for 3 hr.; *B*, heated at 500° C. approximately ½ hr., quenched in water and measured soon after quenching; *C*, heat treated same as *B*, aged at room temperatures for about 1 week; *D*, heat treated same as *B*, hardened at 160° C. to maximum tensile strength. Numbers plotted indicate per cent. elongation of test pieces.

1912, found that the hardness of aluminum bronzes may be increased after quenching by tempering at a temperature lower than the quenching temperature.

The first company to conceive the general applicability of the method now called "precipitation hardening" was the Giulini Works. By its Swiss Patents No. 85606 and No. IUIOO, Dec. 1, 1916, and Feb. 5, 1918, and in many foreign patents, it patented the process of treating metals at a relatively low temperature for obtaining increased hardness,

tensile strength, and workability. As examples in these patents, some aluminum alloys are specified; here also the necessary condition of treat-

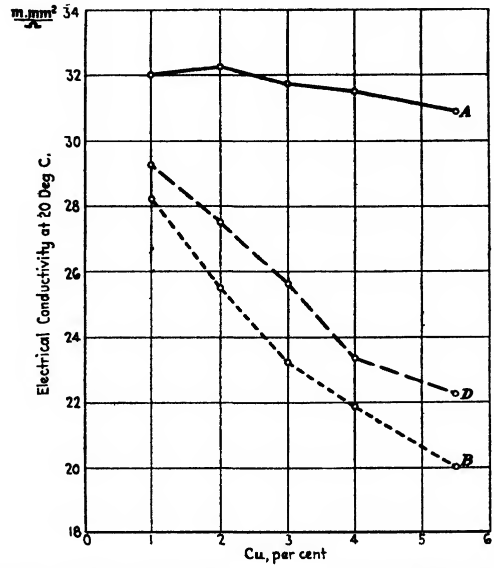

FIG. 12.—EFFECT OF COPPER ON THE ELECTRICAL CONDUCTIVITY* OF ALUMINUM CONTAINING APPROXIMATELY 0.6 PER CENT. SILICON AND 0.4 PER CENT. IRON.

A, HEATED AT 300° C. FOR 3 HR.; *B*, HEATED AT 500° C. APPROXIMATELY ½ HR., QUENCHED IN WATER AND MEASURED SOON AFTER QUENCHING; *D*, HEAT TREATED SAME AS *B*, HARDENED AT 160° C., TO MAXIMUM TENSILE STRENGTH.

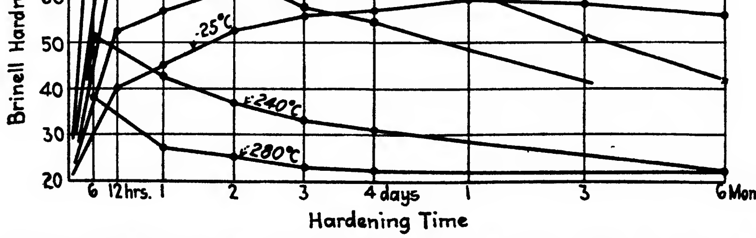

FIG. 13.—EFFECT OF TIME ON HARDNESS OF ALUMINUM, CONTAINING 0.7 PER CENT. MAGNESIUM AND APPROXIMATELY 0.6 PER CENT. SILICON AND 0.4 PER CENT. IRON, HARDENED AT DIFFERENT TEMPERATURES.

ing at higher temperature with consequent quenching, though well known to the Giulini Works, is not mentioned. The Giulini Works

* To get the conductivity in per cent. of the conductivity of International Annealed Copper Standard, multiply the figure in the diagram by 1.724.

developed the method of precipitation hardening and, convinced of its importance for all kinds of alloys, devoted one of the best equipped metallurgical laboratories in Europe to this special research work. At that time, American and French metallurgists also began working on the same problem.

The startling effects obtained by precipitation hardening whereby great changes in physical properties are brought about without showing any microscopic change in the structure led to many explanations. Two allotropic forms of aluminum and chemical reactions produced by the heat treatment had been considered possible. While the metallurgists were seeking for an explanation, the problem was solved from a basis that has often explained many strange phenomena in other fields

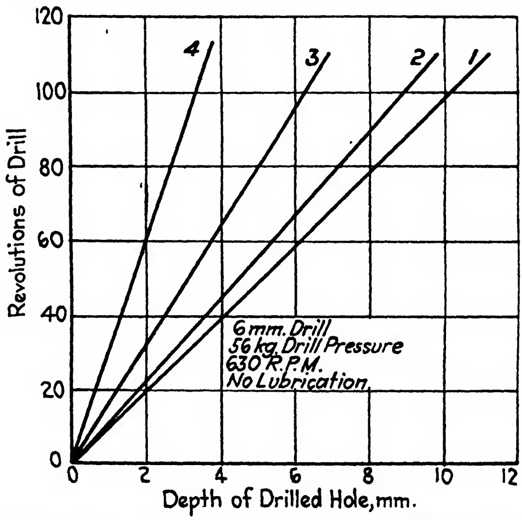

FIG. 14.—WORKABILITY, ACCORDING TO KESSNER, OF: 1, BRASS, WITH SPECIAL HIGH WORKABILITY; 2, ALUMINUM, WITH APPROXIMATELY 3.5 PER CENT. COPPER, 0.5 PER CENT. MAGNESIUM, 0.6 PER CENT. SILICON, AND 0.4 PER CENT. IRON, HARDENED; 3, COMMERCIAL ALUMINUM, AS ROLLED; 4, COPPER, AS ROLLED.

of science, the chemistry of colloids. By the study of colloids it was soon discovered that colloidal solutions, at a certain degree of dispersion, would rapidly increase in viscosity; or, that solid colloids have a maximum strength at a critical dispersion. The use of heat treatment as a means to change the dispersion was also well known. Benedicks seems to have been the first to have decidedly connected colloid chemistry with metallography. In this country, also, the war probably was the cause for the delay in the development of this science and it took some years until the proper solution for the hardening of aluminum alloys by aging was found. The Giulini Works had not found an explanation for the aging of aluminum alloys in 1918, when the writer joined its research staff and was assigned the study of this subject. As an initial step I likened the

hardening of aluminum by silicon and magnesium to the hardening of iron by carbon. The observation that the amount of graphitic silicon, as shown by the analysis of commercial aluminum and special aluminum-silicon alloys, depends on heat treatment brought Bosshardt to a colloid chemical conception of these phenomena.[9] A further study of colloid chemical literature and the investigations of Merica, Waltenberg, Scott and Freeman and Alexander in the hardening of duralumin verified this theory. Jeffries and Archer have restricted the general colloid theory to the slip interference theory. The latter may be in accordance with the true phenomenon, but it should be borne in mind that also in non-crystalline bodies the degree of dispersion plays a similar role, just as in the crystalline metals. As examples, I might mention the increase of viscosity in colloidal fluid solutions and the hardening of rubber by the colloidally dispersed sulfur during the vulcanization.

The authors state that the precipitated particles remain submicroscopic even after a treatment at 300° C. This is true if heat treatment is not of long duration; after a heat treatment of one year or more, the particles had grown so much that Bosshardt found them visible under the microscope. As the authors did not publish tables or curves showing the properties of alloys in the vicinity of the described ones, some curves are given here which will show how tensile strength and the elongation vary with the composition.

These results were found by the systematic study of the alloys. Tensile strength and elongation may often be increased by a careful selection of temperatures and time of heat treatment. When running these tests, temperatures and time had been standardized as indicated on the diagrams. The specimens, about ¼ in. in diameter, were obtained by rolling and drawing an ingot about 2 in. in diameter. The elongation was measured on a length of 25 cm. (except in Fig. 10, where the measured length is ten times the diameter). It is therefore not possible to compare the figures given in the diagrams with the figures of the authors. In general, the elongation measured on an American (4 × diameter) standard test piece would be much greater than the elongation found on a test piece having a measured length about forty times its diameter, especially when the cylindrical elongation is small; that is, when the elongation unaffected by the contraction near the rupture is small, as in the case of hardened test pieces. The elongation measured along a

[9] Making use of the knowledge that silicon is soluble in aluminum at higher temperatures we were able to shorten greatly the analysis by treating the specimen for about 1 hr. at temperatures between 550° and 600° C. followed by sudden quenching in water to room temperatures. At the high temperature, the silicon is dispersed in the aluminum in molecular form, and by dissolving the aluminum in acids or alkalies, the silicon dissolves completely. Any complication on account of graphitic silicon is thus avoided.

great length (in proportion to the section of the test piece) usually gives a better idea of the forming qualities than the elongation measured along a short length. The statements of the authors regarding heat treatment and strength of these alloys and these curves will be found in agreement.

The paper made only a slight mention of the electrical properties of these alloys. Matthiessen, Le Chatelier, and others showed that the electrical conductivity decreases very much with the formation of solid solutions. Therefore the aluminum alloys under consideration have their greatest conductivity after a treatment at about 300° to 350° C., where the greatest amount of the dissolved Mg_2Si, $CuAl_2$, etc. can be precipitated. The solubility at lower temperatures is smaller, but the molecular friction at these temperatures is so great that a complete precipitation cannot be obtained. On the other hand, the minimum conductivity is found after quenching from a temperature where all copper, magnesium, silicon, etc. are in solution. During the precipitation hardening, the conductivity generally rises (we know some cases where it falls slightly just after quenching); usually it becomes somewhat greater than after the quenching from the higher temperature, but when hardened below about 200° C. it will never reach the maximum value obtained at 300° to 350° C. However, it is possible, under certain conditions, to increase the conductivity of the aluminum-magnesium-silicon type close to its maximum value by treatment at temperatures where such an increase would not be possible under ordinary conditions. This is shown in Fig. 12.

A question of great importance is the stability of the hardened alloys at elevated temperatures. The paper mentions a test covering 60 days. This period is not long enough to decide the stability at temperatures below 160° C.; Fig. 13 shows that even at as low a temperature as 130° C. the hardness decreases at the rate of 24 per cent. in half a year; at 160° C. this rate is 55 per cent. Tests covering a long time should be made for each of the commercial alloys previous to putting it in service at temperatures above 100° C. The softening rate may change with the composition of the alloy, but the general character of the softening will, probably, always be the same.

The workability by cutting tools can be determined with the drill hardness machine, according to Kessner; Fig. 14 gives the results of tests made with this machine. The tests show that the workability of the hardened aluminum-copper-magnesium-silicon alloy (3.5 per cent. copper, 0.5 per cent. magnesium, 0.6 per cent. silicon) is nearly the same as that of a brass specially suitable for working by cutting tools.

Further work in the Giulini Laboratory revealed that many other alloys besides aluminum alloys can be hardened by the precipitation method. Mr. Bosshardt and the writer studied all the published binary

equilibrium diagrams. In nearly every instance where such a diagram showed a decrease of solubility of one constituent in the other, the method of precipitation hardening is applicable; but in general the effect may be increased by adding a suitable third element. However, very often where the microscope and the thermoanalytical method fail to reveal a change in solubility, the method of precipitation hardening will show a change. In the metallographical analysis of alloys, therefore, this method should be used in addition to the usual well-known methods.

With this high-strength aluminum alloys, a period will start in the field of non-ferrous alloys similar to the development of the alloy steels in the steel industry. May it be as successful.

Robert S. Archer and Zay Jeffries (authors' reply to discussion).—Both Doctor McAdam and Mr. Knerr have discussed, at some length, certain factors that affect the substitution of strong aluminum alloys for other materials of construction for the purpose of reducing weight. Mr. Knerr has discussed this question from the standpoint of specific tenacity, while Doctor McAdam has considered specific endurance limit, taking into consideration not only simple tension but bending and torsion. But there are involved in the use of the strong aluminum alloys for the purpose of reducing weight other factors, which sometimes entirely overbalance specific tenacity and specific endurance. For example, the controlling factor in design is rigidity, or stiffness in the sense of resistance to deflection, under loads within the elastic limit. This property is determined by the size and shape of the part and by the elastic modulus of the material. The elastic moduli of the various structural metals and alloys are substantially independent of heat treatment and mechanical treatment and are characteristic of the chemical composition involved. Young's modulus for all steels, for example, may be taken as 30,000,000 lb. per sq. in.; while for aluminum alloys, it is 10,000,000 lb. per sq. in. Frequently, when the sections necessary for the required stiffness have been provided, the strength and endurance properties are more than ample. In such cases, it is generally possible to make a material saving in weight by using the strong aluminum alloys. Those interested in this question can obtain illustrations of this point by a few simple calculations of the stiffness of various beams.

Another advantage of the light alloys, which is frequently important, is the greater ease and certainty of producing and handling thin pieces. For example, the sheet used in forming the structural members of aircraft is often quite thin, even in the aluminum alloys; suposing it to be possible to obtain equivalent stiffness and strength with the same weight in high tensile steel, the steel sheet would be objectionably thin. Similar considerations sometimes apply in the case of heavier parts, like forgings, where in order to take full advantage of the greater strength and higher

elastic modulus of steel it would be necessary to forge impractically thin sections. The larger sections involved in aluminum design are more easily formed and slight errors in dimension are of less importance than they would be in the case of the thinner steel sections.

The authors have mentioned two factors affecting the use of the strong aluminum alloys in structural parts where the saving of weight is the primary object. Of course, often, other objects may be more important, such as greater economy of production or the superior finish and appearance of wrought aluminum. Where these or any other of the specific characteristics of the aluminum alloys, other than lightness, form the primary reason for the use of aluminum, it is often true that the specific tenacity and specific endurance of the aluminum alloys are sufficiently high to cause no concern.

Doctor McAdam has referred to the work of the National Physical Laboratory, as exemplified in the Eleventh Report to the Alloys Research Committee. The results published in the Eleventh Report on artificial aging (that is, aging at temperatures above room temperature, of aluminum alloys) are of a rather preliminary and superficial nature. The use of longer times and lower temperatures is not merely a matter of securing better control, as Doctor McAdam has suggested, but the results are superior to those obtainable by short-time aging at the higher temperatures to an extent that is quite important. This information on the aging of aluminum alloys was obtained in substantially its present state in the laboratories of the Aluminum Company of America prior to the publication of the Eleventh Report, or any other publications of which the authors have knowledge.

Doctor McAdam has also called attention to the diagram of the National Physical Laboratory showing the solubility of copper in solid aluminum; this diagram is inaccurate, as will be shown in a forthcoming contribution from the laboratories of the Aluminum Company of America.

Mr. Schweizer has contributed some results, previously unpublished so far as the authors are aware, of investigations at the Giulini Works. In general, these results are in agreement with those obtained in the laboratories of the Aluminum Company of America, although there are some discrepancies as to detail. In Fig. 13, for example, a curve shows a decrease in hardness after aging for more than one month at 25° C. (room temperature) for an alloy containing 0.7 per cent. magnesium and 0.6 per cent. silicon; the authors have not obtained any indication of a decrease in hardness on prolonged aging at room temperature in any of the alloys under discussion.

As to the development of the theory of age hardening or precipitation-hardening, it may be pointed out that Scientific Paper No. 347 of the Bureau of Standards, by Merica, Waltenberg, and Scott, in which their

theory is fully disclosed, is signed Feb. 27, 1919. This theory was undoubtedly developed during 1918, or earlier, at which time, according to Mr. Schweizer, "the Giulini Works had not found an explanation for the aging of aluminum alloys." It therefore seems clear that to Merica and his co-workers belongs the credit for advancing the first rational explanation of this phenomenon.

There is now little question that "age hardening" is caused by the precipitation of finely divided or "colloidal" particles. There is some difference of opinion, however, as to whether these particles exert their hardening effects primarily by mechanical obstruction to slip or by surface forces, or other specific forces such as would increase the hardness of a non-crystalline aggregate. The former view was advanced by the present authors in 1921, and is still held by them after considering subsequent evidence and discussion. Probably the developments of the next few years in metallography and molecular physics will make it possible to draw conclusions with more certainty.

Casting and Heat Treatment of Some Aluminum-Copper-Magnesium Alloys

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(Milwaukee Meeting,§ October, 1924)

The wrought alloys of aluminum with small amounts of copper and of magnesium have, with the development of the automotive and aircraft industries, sprung into prominence through the medium of duralumin; but the cast alloys remained in the background because their possibilities in the heat-treated condition were either not recognized or not fully investigated. In 1919, the Bureau of Standards published a preliminary survey[1] of this field, which pointed out that, in general, the ultimate strength and the percentage of elongation of the alloys of aluminum with and without magnesium could be improved by so simple a treatment as heating at 932° F. (500° C.) for 2 hr., cooling in air, and aging at room temperature for several days. British investigators, too, working with chill-cast material, found that "considerable improvement in the mechanical properties of copper-aluminum alloys may be obtained from suitable heat treatment applied to castings."[2] Jeffries and Gibson[3] made the first contribution to the literature dealing exclusively with the heat treatment of sand-cast aluminum-base alloys, describing the effect of small additions or of combinations of copper, magnesium, and iron on the response to a short heat treatment comprising heating at 932° F. in a nitrate bath for 1 hr., quenching in fish oil, and reheating at 300° F. for for 1 hr. Their results disclosed the facts that the ultimate strength and the percentage of elongation of sound alloys were usually, and quite uniformly, improved by heat treatment; that with the iron content ranging between 0.36 and 0.88 per cent. and the silicon content between 0.24 and 0.60 per cent. the effect of increasing the copper content (Tables 10

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[1] Merica and Karr, Bureau of Standards *Tech. Paper* 139 (1919) 11.

[2] Inst. Mech. Engr., Eleventh Report to the Alloys Research Committee (1921), 39–41.

[3] The Heat Treatment of Aluminum-Alloy Castings. *Trans.* (1921) 64, 270.

and 11) is erratically to increase the ultimate strength and to lower the percentage of elongation in both the cast and the heat-treated alloy; and that the effect of the heat treatment is uniformly to improve, by about 20 per cent., the strength and ductility of the sand-cast alloy. They further showed that for alloys with copper content varying from 3 to 6 per cent. and iron in amounts at least up to 1.4 per cent., the effect of heat treatment is to preserve, as a minimum, the percentage of elongation of the alloy as cast and to increase substantially the ultimate strength; that the addition of iron is more beneficial to aluminum alloys low in copper than those high in copper; and that the effect of magnesium additions to an alloy containing 3 per cent. of copper and 1.4 per cent. of iron is to increase practically continuously the ultimate strength of the alloy both as cast and as heat treated, more especially that of the heat-treated alloy (which has a maximum of about 37,000 lb. per sq. in. and an elongation of about 1.3 per cent. at 1.1 per cent. of magnesium); and to decrease continuously and in about the same proportion the percentage of elongation of both the cast and the heat-treated alloy, from approximately 7 per cent., with no magnesium, to about 1.5 per cent., with 1.4 per cent. of magnesium.

The present paper deals with a portion of the work of the Materials Section, Engineering Division, Air Service, U. S. A, on the casting and the extended heat treatment of alloys of the duralumin type (copper, 2.5–5.0 per cent.; magnesium, 0.0–1.0 per cent.; silicon, 0.2–1.0 per cent.; iron, 0.3–1.5 per cent.; manganese, 0.0 to 1.0 per cent.; chromium, etc.). This range of compositions includes an alloy recently placed on the market in the cast form and designated as Lynite 195.

Methods of Alloying

The composition of the raw materials used in the manufacture of the various alloys is shown in Table 1. Aside from the aluminum-manganese alloy, all of the hardeners were made in the McCook Field foundry by the following methods:

For the aluminum-copper (50:50) hardener, all the copper (under charcoal) and one-half the aluminum (with no cover) are melted separately in plumbago crucibles. The copper is then skimmed and poured into the molten aluminum; this causes a rapid rise in temperature, which is checked by the addition, in small pieces, of the remainder of the solid aluminum ingot. This aluminum-copper hardener is very brittle and is easily broken for accurate weighing.

The aluminum-iron (94:6) hardener is made by soaking wrought iron into aluminum at about 1700° F., zinc chloride or a mixture of cryolite and salt being used as a flux. The time required to melt the nails is about 1 hr., but the hardener is uniform and free from iron oxide, which

TABLE 1.—*Composition of Raw Materials*

Metals

Melt No.	Copper, Per Cent.	Silicon, Per Cent.	Iron, Per Cent.	Magnesium, Per Cent.	Manganese, Per Cent.
			Aluminum Ingot		
593	0.07	0.20	0.25		
1045	0.21	0.45	0.46		
1661	0.07	0.14	0.32		0.01
1662	0.32	0.30	0.82		0.04
1799	0.02	0.36	0.38		
2063	0.02	0.14	0.29		
			Magnesium		
919	Stick			99+	
2013	Slab			99+	
			Hardeners		
			Aluminum-copper		
1006	49.55	0.17	0.29		
1605	47.69	0.22	0.65		
1872	59.40	0.19	0.38		
2239	49.70	0.19	0.33		
2548	49.59	0.23	0.27		
			Aluminum-iron		
253			6.00		
			Aluminum-manganese		
1817	0.40	0.50	0.78		6.99
			Aluminum-silicon		
2415		18:45	0.48		
			Aluminum-copper-iron		
1851	22.30	0.38	15.7		
1857	23.49	0.27	15.73		
2527	25.38	0.30	13.23		

forms when the iron is melted by itself or is alloyed with aluminum at very high temperatures. This hardener is not particularly brittle, but it was used in the alloys described in this paper. At present, a 33 per cent. iron alloy made in the same way as the 6 per cent. alloy and much more easily broken, is being used.

For the aluminum-silicon (80:20) hardener, the silicon and an equal weight of aluminum ingot are charged and melted together at 1800° F. The rest of the aluminum is added, either in solid pieces or molten. No fluxes are used. This hardener is quite tough and must be sawed into small pieces. (An easily broken 50:50 hardener is available commercially.)

For the aluminum-copper-iron (62.5:25.0:12.5) hardener, the aluminum and copper are charged and melted together. Small pieces of wrought iron are then soaked into the alloy held at a temperature of from 1600 to 1800° F. Another method consists of charging wrought iron with copper and melting the copper only. The aluminum is melted in another crucible and is poured into the copper; the wrought iron alloys completely from the heat of the reaction. No fluxes are used. This hardener is very brittle and lends itself to accurate weighing.

All of these alloys should be thoroughly stirred before pouring and should be pigged in cast-iron molds. In general, the hardeners should be poured into thin section, to facilitate breaking and to prevent segregation, especially in the iron-bearing mixtures.

In founding alloys of the duralumin type, the aluminum ingot is simply charged and melted with the necessary hardeners in a plumbago crucible, the fuel being either oil or gas. If the melt requires magnesium, the crucible is withdrawn from the furnace and then the magnesium is added, in solid form, by plunging it below the surface of the molten charge and holding it there until complete solution has taken place. No trouble is experienced from loss of magnesium. Fluxes and covers are not used in the routine practice, although some experimental work has been carried out in this direction. Bare chromel-alumel thermocouples and the Leeds & Northrup potentiometer are used to control the maximum furnace (about 1425° F.) and the pouring temperature.

Methods of Casting

Alloys of the duralumin type, both high and low in copper, are slightly more difficult to cast than the conventional 8 per cent. copper (aluminum) alloy. The solidification range of the former, which tend to act like a pure metal, is more narrow than that of the latter, in which the large amount of liquid eutectic serves to keep the alloy pasty for some time and assists in the conformation of the metal to the mold and core outlines. The very phenomenon that promotes ease of casting leads to the disadvantages of segregation and porosity, induced by the draining of the eutectic from

about the already solid aluminum-rich crystals. The theoretical aspects of the mechanism of solidification of the aluminum-copper alloys have been thoroughly discussed by J. D. Edwards.[4] From the practical standpoint, McCook Field results have shown that test specimens machined from the same locations in large castings possess comparative uniformity of physical properties when of duralumin high in copper (4.5 per cent.) and considerable heterogeneity when of the 8 per cent. copper alloy.

The foundry practice for the alloys of the duralumin (Al-Cu-Mg) type is similar to that for the magnalite (Al-Cu-Ni-Mg) type, except

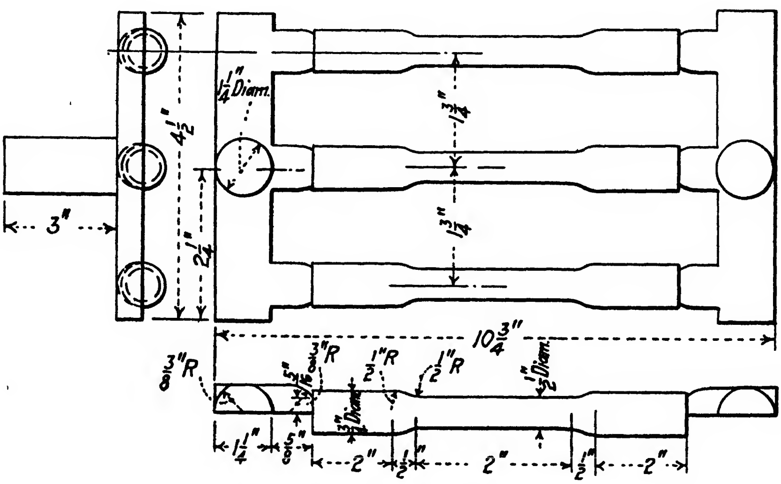

FIG. 1.—TENSION SPECIMEN AS CAST.

that the latter more frequently requires chills even in heavy uniform sections.[5] Complicated castings in duralumin have been made, with relatively heavy risers or feeding heads, where it was necessary to place chills only in abrupt changes of section. An interesting use for the duralumin low in copper has been in parts that not only must be cast with extreme changes in section, but must be impervious. The 10 per cent. copper alloy had previously been used for this purpose.

The range of pouring temperatures used for duralumin was from 1250° to 1300° F. Most of the castings and all test specimens, which were cast to size three to the mold as shown in Fig. 1, were poured from 1300° F. into green Albany sand. The chemical composition and the physical properties of a number of alloys so cast are given in Table 2.

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[4] Mechanism of Solidification of a Copper-Aluminum Alloy. *Chem. & Met. Eng.* (1921) **24**, 217.

[5] Lyon and Daniels: Notes on a Sand-cast Aluminum-Copper-Nickel-Magnesium Alloy. *Jnl.* Soc. Automotive Engineers, (1924) **14**, 173.

An investigation of mold materials showed that the chilling effect of metal molds could not be approached by the use of carborundum, fire sand, or other highly refractory materials. Drying the sand molds decreased the rate of cooling of the metal, imparting to it a coarser crystalline structure. Table 3 shows the relationship between the physical

TABLE 2.—*Composition and Physical Properties of Some Al-Cu-Mg(Mn) Alloys as Sand Cast*

Melt Number	Ultimate Strength, Lb. per Sq. In.	Elongation in 2 in., Per Cent.	Brinell Hardness Number	Specific Gravity	Composition				
					Copper, Per Cent.	Magnesium, Per Cent.	Silicon, Per Cent.	Iron, Per Cent.	Manganese, Per Cent.
341					4.47	0.12	0.57	0.51	
1088	23,790	2.2	50	2.75	4.10	0.97	0.52	1.08	Trace
1167	21,390	2.0	54	2.73	3.98	0.57	0.47	0.60	Trace
1401					4.35	0.71	0.46	0.72	
1844	19,880	1.0	61	2.77	4.65	0.47	0.30[a]	0.60[a]	
1862	19,700	1.7	54	2.75	4.00[a]	0.13	0.30[a]	0.60[a]	
1863[a]	18,280	0.8	70	2.75	4.00	0.60	0.30	0.60	
1864[a]	19,230	1.2	65	2.76	4.00	0.60	0.30	0.60	0.75
1882[a]	16,540	3.5	46	2.70	2.00	0.50	0.25	0.40	
1883[a]	21,700	2.2	63	2.73	3.50	0.75	0.25	0.40	
1884[a]	18,760	1.2	61	2.75	4.00	0.50	0.25	0.40	
1885	19,880	2.5			3.11	0.50	0.24	0.41	
1886[a]	20,580	1.0			4.00	0.50	0.25	0.40	0.75
1887[a]	20,210	1.7	60	2.74	3.00	0.50	0.25	0.40	0.75
1888[a]	19,200	2.8	50	2.71	2.00	0.50	0.25	0.40	0.75
1903	24,080	6.5			2.08	0.41	0.28	1.18	
1904	23,830	1.5			3.96	0.40	0.24	1.12	
1905	25,280	3.0			3.04	0.38	0.26	1.18	
2263	18,550	2.0			4.63	0.22	0.47	0.95	
2266					Remelt of melt 2263				
2307	21,100	4.5			4.45		0.91	0.98	
2310	21,430	2.0			Remelt of melt 2263				
2312[b]	19,800	3.7			Remelt of melt 2307				
2313[b]	17,260	2.3			Remelt of melt 2263				
2536	20,200	2.2			4.35	0.22	0.52	0.95	
2702	17,850	4.2			4.57	0.10	0.45	0.55	0.11
2711	20,760	2.0			4.87	0.31	0.56	0.75	
2711[b]	23,290	2.0							

[a] Calculated analysis. [b] Chill cast.

properties of the cast and those of the heat-treated alloy containing 4.35 per cent. copper and 0.22 per cent. magnesium, cast in green and in dry Albany sand, in carborundum sand molds, and in cast-iron molds. In the alloy as cast, the mold material affected the ductility principally. Metallographic analysis showed that this effect was attributable to the

TABLE 3.—*Effect of Mold Materials on Tensile Properties*[a]

(Melt 2536)

	Albany Molding Sand				Carborundum Fire Sand				Cast-iron Mold			
	Green		Dry		Green		Dry		Mold Temp. 450° F.		Mold Temp. 850° F.	
	As Cast	H.T.[b]	As Cast	H.T.	As Cast	H.T.	As Cast	H.T.	As Cast	H.T.	As Cast	H.T.
Ultimate strength, lb. per sq. in.	22,450	34,850	19,790	30,210	23,520	33,620	21,200	32,920	22,100	38,040	24,130	35,460
Elongation in 2 in., per cent.	2.3	4.2	1.5	2.6	4.0	4.0	3.0	3.5	2.5	6.4	2.8	4.1
Number of specimens tested	5	9	16	3	2	1	2	1	6	6	3	4

[a] Pouring temperature 1300° F.

[b] Heat treatment: 96 hr. at 925° F., quenched in cold water, and aged at 300° F. for 8 hr.

rate of cooling rather than to any reaction of the molten metal with the mold material. Heat treatment equalized small differences in the properties of the alloy as cast and as influenced by the mold material and its condition, particularly in the case of sands. The beneficial effect of chill casting was much more evident after heat treatment than before.

From the foundry standpoint, neither permanent molds nor carborundum-sand molds are practicable. The use of the former is much restricted because of the cost of making molds; and carborundum sand is more expensive than the ordinary molding sands and produces a decidedly inferior surface on the casting. Dry sand molds made from carborundum sand are very hard and generally cause the test specimens to pull away from the risers. This condition may be improved by using higher proportions of heap sand as a binder, but the advantage to be gained from the superior conductivity of the carborundum sand is lost in the dilution. All things considered, a grade of molding sand of the Albany type is the most desirable for general use.

Methods of Testing

As cast or as heat treated (Tables 2 to 12, inclusive), the test specimens were pulled between wedge grips in a 20,000-lb. Olsen machine; and after rupture the percentage of elongation was determined by fitting the broken bars together as closely as possible and measuring the extension to the nearest 0.01 in. Each average in the tables is that of three specimens, except in Table 12, where the average may represent as many as eighteen test specimens. The Brinell hardness values, for a 500-kg. load and 10-mm. ball, were taken on broken tension specimens. The results given in Table 10 were obtained from a series of Brinell hardness tests made periodically on the same bar, the values accordingly representing but one Brinell impression. The specific-gravity determinations were made by the ordinary displacement method. All tests were made seven days after the completion of heat treatment, unless otherwise specified.

Methods of Heat Treating

Most of the heat-treatment experimentation was designed to determine the behavior of the cast duralumins high in copper, without and with magnesium in amounts up to 0.3 per cent. The following factors were investigated: Effect of quenching temperature; effect of time at quenching temperature; effect of aging temperature; effect of time at aging temperature; and effect of reheating following quenching and aging. Such considerations as the nature and temperature of the quenching medium were not explored thoroughly. The nitrate bath as a heating medium was used but it was abandoned for many reasons, among which were the

occasional formation of exudations on the surface of the castings and the contamination of the quenching medium. The electric furnace, automatically controlled to within ±10° F., gives a remarkable uniformity of physical properties for a specific heat treatment and possesses none of the disadvantages inherent in the nitrate bath. It is not believed that heated alloys suffer mentionable decomposition and deterioration when quenched in water, as reported by Jeffries and Gibson.[6] Some reaction may take place in the quenching medium, but it is secondary and minor in consequence. Discolorations in fractures quite generally result from oxidation, which occurs in the heating before quenching. They may be prevented, at least to a large degree, by a sodium-silicate treatment developed at McCook Field. Aging was accomplished in air at room temperature, in boiling water, or in an automatically controlled electric oven when the temperatures were to be between 300° and 500° F. A large percentage of the results included in the accompanying tables was obtained from test specimens heat treated with castings used in aircraft construction.

Physical Properties

Cast Alloys

Analysis of the results shown in Tables 2 and 3 indicates that whether sand or chill cast the high-copper duralumin with the magnesium content up to 0.15 per cent. developed an ultimate strength ranging from 18,000 to 21,000 lb. per sq. in. and an elongation of from 2.0 to 4.5 per cent. With further increase of magnesium up to 0.33 per cent., the ultimate strength was not appreciably affected but the elongation was decreased to about 2 per cent.

In the sand-cast low-copper duralumins, Table 12, in which the content of magnesium was kept constant at 0.40 per cent., that of iron at 1.25 per cent., and that of silicon 0.25 per cent., the ultimate strength for copper contents between 2 and 3 per cent. was about 25,000 lb. per sq. in.; but the elongation fell from 6.5 per cent., for the 2 per cent. copper alloy, to 3 per cent., for the 3 per cent. copper alloy. Increasing the copper to 4 per cent. caused a drop in the elongation to 1.5 per cent.

These figures show that the best combination of strength and ductility in these alloys, as sand cast, resulted from the following analysis: Copper 2.5 per cent., magnesium 0.5 per cent., iron 1.25 per cent., silicon 0.25 per cent. It is to be observed that the composition of the alloy requires that a high-grade aluminum ingot be used for its manufacture, and that most of the iron be introduced in the form of an aluminum-iron hardener.

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[6] *Loc. cit.*, 271.

Cast and Heat-treated Alloy

The effect of quenching temperature on the high-copper duralumins was determined from test specimens soaked for 96 hr. (which period gives an approximation of equilibrium conditions), quenched in cold water, and aged at 300° F. for 8 hr. Table 4 and Fig. 2 show that, for the sand-cast alloys, the best combination of strength and ductility for this treatment was secured by quenching from 950° F. The chill-cast material, however, responded to heat treatment erratically, the best properties (ultimate strength of 47,500 lb. per sq. in. and elongation of 8 per cent.) resulting from a temperature of 1010° F., very close to its initial melting point (solidus). Close control of the heating and quenching temperatures is imperative. For sand-cast material, quenching temperatures below 925° F. give inferior results; while temperatures in excess of about 1000° F. cause the alloy to be very fragile and exceedingly inferior in physical properties even after aging.

TABLE 4.—*Effect of Quenching Temperature*

(Specimens soaked for 96 hr. at indicated temperature, quenched in cold water, and aged at 300° F. for 8 hr.)

Quenching Temperature, Degrees F.	Ultimate Strength, Lb. per Sq. In.			Elongation in 2 In., Per Cent.			Brinell Hardness Number		
	SC[a] Melt 2702	SC Melt 2711	CC Melt 2711	SC Melt 2702	SC Melt 2711	CC Melt 2711	SC Melt 2702	SC Melt 2711	CC Melt 2711
850		33,010			2.0			74	
875	30,820	30,500		1.0	2.8				
900	24,030	30,650	31,790	2.0	2.5	3.5			
925	38,580	35,870	44,540	1.0	3.2	7.5	93	74	
950	44,100	37,010	42,550	1.0	3.2	5.7	86	80	83
975	43,750	34,300	39,600	1.0	3.5	4.7	96	74	80
1,010	6,430	30,210	47,650	0.8	1.5	8.3	89	70	80
1,025		11,800			1.0				
As cast	17,850	20,760	23,290	4.2	2.0				

[a] SC = Sand cast; CC = Chill cast. Pouring temperature, 1250° F.; mold temperature, 550 to 650° F.

It is not to be inferred from this discussion that aging for 8 hr. at 300° F., an arbitrary treatment, produces the most desirable combination of strength and ductility. In fact, there is much to indicate that the physical properties are highly dependent on the composition of the alloy, quenching temperature, time at quenching temperature, aging temperature, time at aging temperature, and possibly the nature and temperature of the quenching medium.

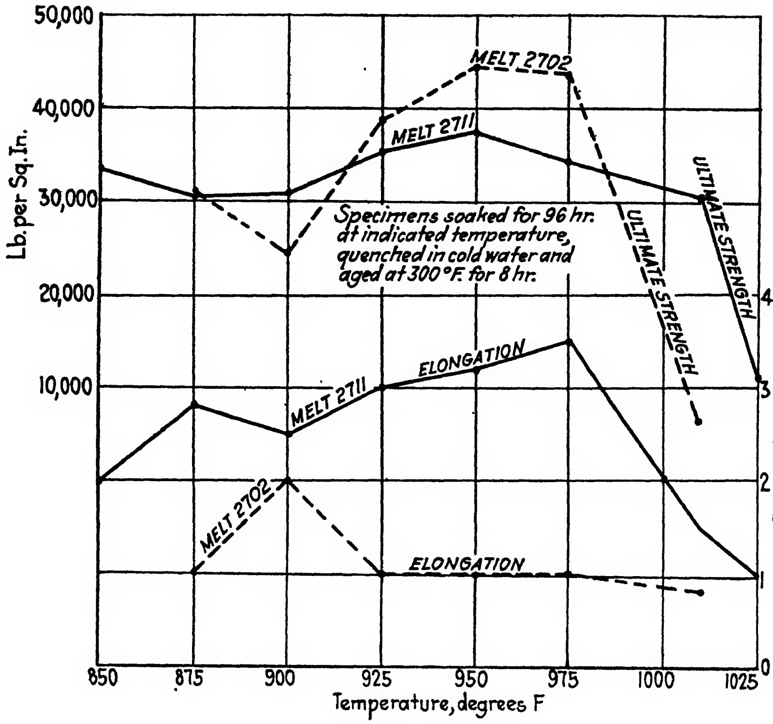

FIG. 2.—EFFECT OF QUENCHING TEMPERATURE.

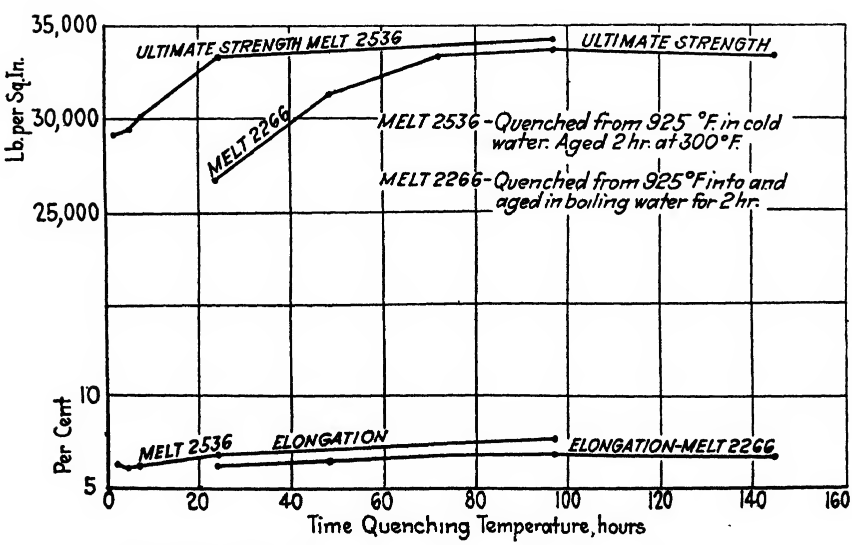

FIG. 3.—EFFECT OF TIME AT QUENCHING TEMPERATURE.

Table 5 and Fig. 3 demonstrate that it is necessary to soak for 96 hr. (at a minimum temperature of 925° F.) in order to obtain the best combination of strength and ductility. Metallographic analysis has shown that to obtain the maximum strength or ductility it is necessary to get all of the $CuAl_2$ compound into solution before quenching. Inasmuch

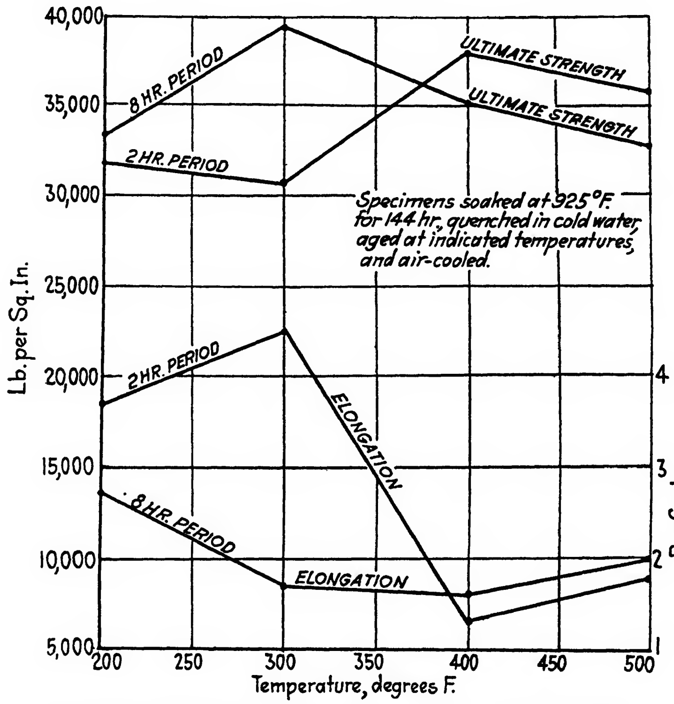

FIG. 4.—EFFECT OF AGING TEMPERATURE, MELT 2266

as the 96-hr. soaking at 925° F. accomplished this and as the rate of solution increases with temperature, it is entirely probable that at about 950° F. the period of soaking could be diminished. This relationship of temperature to time on the rate of solution of $CuAl_2$ is being worked out. Table 5 also shows that the cold-water quench followed by aging at 300° F. for 2 hr. produced better results than quenching into and aging in boiling water for 2 hr., more especially from the standpoint of ductility.

The effect of aging temperature is shown in Table 6 and Fig. 4. For the 2-hr. period of aging at temperatures between 200° and 500° F., the aging temperature of 300° F. produced the best combination of strength and ductility. Aging temperatures in excess of 300° F. (for a period of 2 hr.) caused a rapid increase in strength at the sacrifice of ductility. Too much importance cannot be attached to the necessity for securing the

proper relationship between aging temperature and time at aging temperature, which effect will presently be considered.

TABLE 5.—*Effect of Time at Quenching Temperature (of 925° F.) for Various Periods of Aging at 300° F.*

(Specimens quenched in cold water unless otherwise stated)

Time at Quenching Temperature, Hours	Melt 2536								Melt 2266	
	Ultimate Strength, Lb. per Sq. In.				Elongation in 2 In., Per Cent.				Ultimate Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.
	Aging Period, Hours				Aging Period, Hours				Quenched into and Aged in Boiling Water	
	2	4	6	8	2	4	6	8	2 Hr.	
2	29,450	29,160	30,570	30,610	2.5	2.5	1.8	2.2		
5	29,470	28,480	27,530	30,470	2.2	1.7	1.7	1.8		
7	30,170	30,260	31,330	31,750	2.7	2.7	2.2	1.8		
24	33,270	32,740	33,130	33,090	3.7	2.9	3.4	2.8	26,700	2.5
48									31,010	3.0
72									33,180	3.5
96	34,690	34,000	36,430	35,990	5.2	4.4	5.0	4.5	33,560	3.7
144									33,210	3.2

TABLE 6.—*Effect of Aging Temperature*

(Specimens soaked at 925° F. for 144 hr., quenched in cold water, aged at indicated temperatures, and air-cooled)

Aging Temperature, Degrees F.	Melt 2266			
	Ultimate Strength, Lb. per Sq. In.		Elongation in 2 In., Per Cent.	
	Aging Period, 2 Hr.	Aging Period, 8 Hr.	Aging Period, 2 Hr.	Aging Period, 8 Hr.
70[a]	22,800		5.3	
200	31,590	33,100	3.7	2.7
300	30,730	39,340	4.5	1.7
400	37,950	35,290	1.3	1.6
500	35,850	32,570	1.8	2.0

[a] Air-cooled from 925° F. and aged at room temperature (70° F.).

Most of the work described in this paper has centered around the aging temperatures of 212° and 300° F.; Table 7 and Fig. 5 permit an intimate study of the changes that occurred, especially for the various

periods of aging at 300° F. In the high-copper duralumin containing (probably inclusively when manganese is absent) up to 0.2 per cent. of magnesium, it was possible to secure an ultimate strength of 28,000 to 35,000 lb. per sq. in. with an elongation of from 7 to 4 per cent., with an aging period at 300° F. at from 2 to 8 hr. Comparison of the 8-hr. with the 2-hr. aging period and with the data in Table 6 shows that a marked decline in the percentage of elongation occurs with aging about 8 hr. The evidence is indisputable that for any aging temperature above

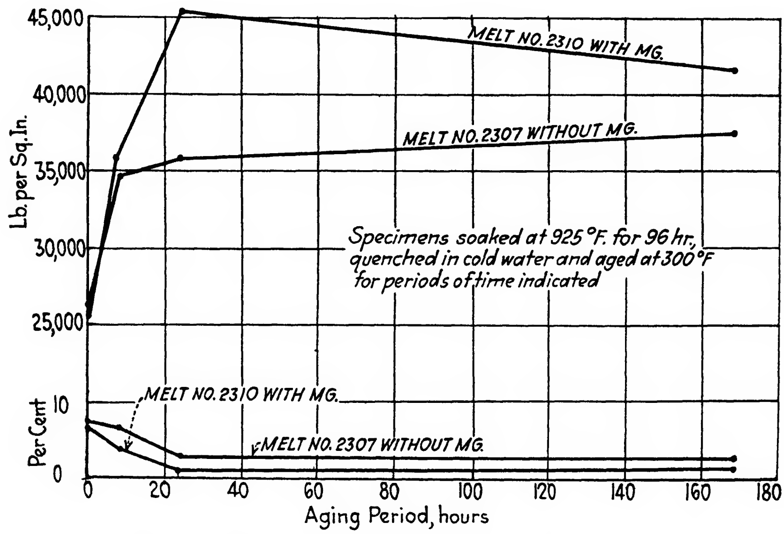

FIG. 5.—EFFECT OF TIME AT AGING TEMPERATURE.

atmospheric up to 500° F. there is a critical aging period, which if exceeded causes an abrupt decline in the percentage of elongation. The position of this point is also dependent on the chemical composition of the alloy, manganese (melt 2702) and magnesium probably in excess of 0.25 per cent. (melt 2711) doubtless shortening the critical aging period. With alloys of the last description, it is necessary to keep within the curtailed aging period to secure the desired higher range of ductility (see melts 2702 and 2711, 2-hr. aging, Table 7).

Aging at 300° F. longer than the critical aging period increases the ultimate strength at the expense of the percentage of elongation. Within 24 hr., generally, the end point (maximum ultimate strength) for the high-copper duralumins is reached, at the end of which time, depending on the composition and the heat treatment previous to aging, there may be obtained a range of ultimate strength of from 35,000 to 45,000 lb. per sq. in.; 50,000 lb. per sq. in. has been secured in individual test specimens. The corresponding range in elongation is from about 3 to 1 per cent. For

TABLE 7.—*Effect of Time at Aging Temperature of 300° F.*

(Specimens soaked at 925° F. for 96 hr., quenched in cold water, and aged at 300° F. for period of time indicated)

Melt Number	Quenched and Tested Immediately		Aging Period											
			2 Hr.		4 Hr.		6 Hr.		8 Hr.		24 Hr.		168 Hr.	
	Ultimate Strength, Lb. per Sq. In.	Elongation, Per Cent.	Ultimate Strength, Lb. per Sq. In.	Elongation, Per Cent.	Ultimate Strength, Lb. per Sq. In.	Elongation, Per Cent.	Ultimate Strength, Lb. per Sq. In.	Elongation, Per Cent.	Ultimate Strength, Lb. per Sq. In.	Elongation, Per Cent.	Ultimate Strength Lb. per Sq. In.	Elongation, Per Cent.	Ultimate Strength Lb. per Sq. In.	Elongation, Per Cent.
2307	25,910	7.5	24,180[a]	6.7					34,630	5.3	35,570	2.8	37,470	2.2
2312	22,850	5.2	26,770[a]	7.0					32,840	5.0	35,240	2.5	38,520	2.0
2702			28,290	6.9					40,980	1.4	43,180	0.8		
2310	25,940	7.0	31,090[a]	3.7					35,900	3.9	45,150	1.0	41,550	1.0
2536			34,690	5.2	34,000	4.4	36,430	5.0	35,990	4.5				
2313	27,740	8.0	38,400[a]	8.7					42,200	8.5	49,230	2.5	46,760	1.7
2711			36,050	4.2					35,870	3.2	44,250	1.2		

[a] Quenched into and aged in boiling water for 2 hr.

the 168-hr. aging period, the results were not appreciably different from those ensuing from the 24-hr. treatment.

Reheating specimens from melt 2310 after they had been quenched and aged for 24 hr., to develop their maximum strength (about 45,000 lb. per sq. in. with an elongation of 1 per cent.), caused a slight loss of strength and minor change in the percentage of elongation when the reheating temperature (quenched in cold water) was 400° and 500° F. (Table 8).

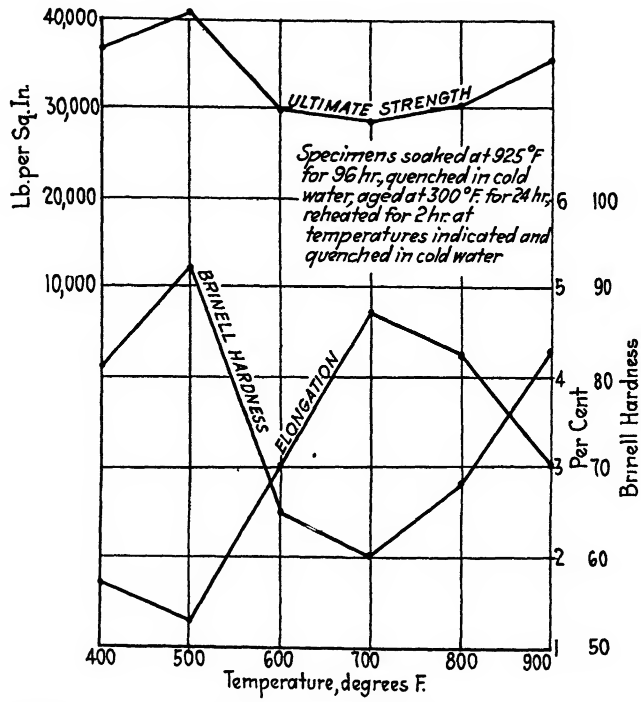

FIG. 6.—EFFECT OF REHEATING AFTER QUENCHING AND AGING, MELT 2310.

When the reheating temperature was 600° F., however, the ultimate strength dropped to 30,000 lb. per sq. in., and the elongation rose to 3.3. per cent. The minimum ultimate strength (28,960 lb. per sq. in.) and the minimum elongation (4.7 per cent.) were obtained with a reheating temperature of 700° F. With higher reheating temperatures (Fig. 6), the softening effect is lost and hardening commences, which increases in intensity with increase in temperature, as was to have been expected. The reason why the alloy on being quenched from 800° and 900° F. develops such a good combination of ultimate strength and percentage of elongation is because the $CuAl_2$ is in a form that goes readily into solution. From practical considerations, the reheating following quenching and

aging is not justifiable on the basis of the resultant physical properties. If the alloy has been heat treated to develop either its maximum strength or its maximum ductility, these data show that the material cannot be subjected to temperatures above 200° to 300° F. in service for any length of time and retain its initial mechanical properties.

TABLE 8.—*Effect of Reheating Following Quenching and Aging* [a]

(Specimens soaked at 925° F. for 96 hr., quenched in cold water, aged at 300° F. for 24 hr., reheated to and for 2 hr. at temperatures indicated, then quenched in cold water)

Reheating Temperature, Degrees F.	Ultimate Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.	Brinell Hardness Number
No reheating	44,060	1.0	102
400	36,110	1.7	81
500	40,680	1.3	92
600	30,000	3.3	65
700[b]	28,960	4.7	60
800	30,500	4.3	68
900	35,670	3.0	83

[a] Melt 2310. [b] Soaked at 700° F. for ½ hr only.

The effect of magnesium, in amounts up to 0.3 per cent., is most apparent in the high-copper duralumins when they are aged at 300° F. (Table 9). When the magnesium content does not exceed about 0.2 per cent., the necessity for aging for periods of less than 8 hr. to retain proper ductility is not so pronounced. If the magnesium content exceeds this figure, or if such elements as manganese are present, the only way to retain the ductility is to limit the aging period to approximately 2 hr. In other words, the critical aging period for an aging temperature of 300° F. depends on what elements are present in the alloy besides copper and, to a less extent, iron and silicon.

In a general way, although no attempt is made to establish a direct relationship, the Brinell hardness appears to be directly proportional to the ultimate strength and inversely proportional to the percentage of elongation (see Fig. 6). Table 10 indicates the stability of the properties of the heat-treated alloys in terms of Brinell hardness. For specimens quenched and aged in boiling water for 2 hr., or for specimens simply quenched in cold water and not aged, the Brinell hardness gradually increases after quenching; the hardness taken 4½ months later is considerably greater than that taken immediately after quenching. When aged at 300° F., however, the alloys assume a stable hardness immediately on completion of aging. Reheating and cold-water quenching after

aging at 300° F. for 24 hr. decreases the hardness from 100 to 49, with a reheating temperature of 800° F., all tests being made ½ hr. after completion of the heat treatment. The Brinell hardness values obtained immediately after reheating and quenching do not change for reheating temperatures up to about 700° F. Beyond 700° F., the gradual hardening effect at room temperature is quite marked in the high-copper duralumin. The Brinell results show that the procedure of testing tension specimens 7 days after aging at 300° F. gives results that are stable.

TABLE 9.—*Effect of Magnesium Additions on Tensile Strength and Hardness*

(Specimens soaked at 925° F. for 96 hr., quenched in cold water, and aged at 300° F. for period of time indicated)

Physical Properties	Melt Number				Heat Treatment
	2307	2702[a]	2310	2711	
	Magnesium, Nil	Magnesium, 0.10 Per Cent.	Magnesium, 0.22 Per Cent.	Magnesium, 0.31 Per Cent.	
Ultimate strength, lb. per sq. in.	25,910		25,940		Quenched only, immediately tested
	24,180[b]	30,110	31,900[b]	35,660	Aged at 300° F. for 2 hr.
	34,630	38,580	35,070	25,200	Aged at 300° F. for 8 hr.
	35,570	43,870	44,060	46,170	Aged at 300° F. for 24 hr.
Elongation in 2 in., per cent.	7.5		7.0		Quenched only, immediately tested
	6.7[b]	7.8	3.7[b]	4.5	Aged at 300° F. for 2 hr.
	5.3	1.0	3.7	3.0	Aged at 300° F. for 8 hr.
	2.8	0.7	1.0	1.0	Aged at 300° F. for 24 hr.
Brinell hardness number	59		60		Quenched only, immediately tested
	55[b]	61	71[b]	74	Aged at 300° F. for 2 hr.
	72	93	82	74	Aged at 300° F. for 8 hr.
	86	96	102	98	Aged at 300° F. for 24 hr.

[a] Manganese, 0.11 per cent. [b] Quenched into and aged in boiling water.

Alloys having an ultimate strength of about 34,000 lb. per sq. in. and an elongation of about 4.5 per cent. usually have a Brinell hardness of from 70 to 80; when the ultimate strength is over 35,000 lb. per sq. in. and the elongation as low as 1.5 per cent., the Brinell hardness is usually greater than 85.

TABLE 10.—*Effect of Heat Treatment on Stability of Alloys as Measured by Brinell Hardness*

(Specimens soaked at 925° F. for 96 hr.)

Heat Treatment	Hours after Completion of Heat Treatment							
	½		24		168		3264	
	Melt No.							
	2307	2310	2307	2310	2307	2310	2307	2310
	Brinell Hardness Number							
None (as cast)			50	61				
925-BW2	52[c]	72[c]	54	76	55	71	64	79
925-CW	57[c]	60[c]	59	80	59	79	64	84
925-CW300-8	71	80	79	82	72	82	78	81
925-CW300-24[a]	88	100	89	110	86	102	87	106
925-CW300-168		105				99	85	104
925-CW300-24-400-2W		82		87		82		85
925-CW300-24-500-2W		92		95		92		89
925-CW300-24-600-2W[b]		66		69		65		65
925-CW300-24-700-2F		40		40		45		43
925-CW300-24-700-½W		55		62		60		62
925-CW300-24-800-2W		49		54		68		71
925-CW300-24-900-2W		54		75		83		84

[a] Quenched from 925° F. in cold water and aged at 300° F. for 24 hr.

[b] Same as [a], but also reheated to and soaked at 600° F. for 2 hr., then quenched in cold water.

[c] Brinell tested 2 hr. after completion of heat treatment.

In Table 11 are grouped the results from a number of miscellaneous heat treatments of high-copper duralumins. Good ductility cannot be obtained with short soakings at the quenching temperature and either the boiling-water or the cold-water quench. The table indicates that for a 2-hr. soaking period, the maximum ultimate strength obtainable is a function not only of time at aging temperature, but of heating (quenching) temperature, much better results having been obtained from 975° than from 925° F. The possibility of increasing the soaking (quenching) temperature to above 925° F. and of shortening the period of soaking has already been considered.

Table 12 gives the data that have been obtained in connection with the development of a low-copper duralumin whose composition is: copper, 2.25 to 2.75 per cent.; magnesium, 0.4 to 0.6 per cent.; iron, 1.15 to 1.35 per cent.; silicon, 0.2 to 0.5 per cent.; aluminum, balance.

TABLE 11.—*Effect of Miscellaneous Heat Treatments on Physical Properties of Al-Cu-Mg Alloys High in Copper*

Heat Treatment	Melt Number	Copper, Per Cent.	Magnesium, Per Cent.	Tested after Completion of Heat Treatment					
				1 Day		3 Days		9 Days	
				Ultimate Strength, Lb. per Sq. In.	Elongation, Per Cent.	Ultimate Strength, Lb. per Sq. In.	Elongation, Per Cent.	Ultimate Strength, Lb. per Sq. In.	Elongation, Per Cent.
925-2BW2[a]	2711	4.87	0.31	28,920	2.1	31,530	1.8	29,950	1.7
925-2BW3	2263	4.63	0.22	28,680	1.5				
925-24BW2				26,700	2.5				
925-2CW300-2				25,130	2.0				
925-2CW300-16				33,430	0.8				
925-2CW300-16-700-2W				22,460	3.8				
975-2CW300-16				41,360	0.5				
925-5CW300-20				34,630	0.5				

[a] Soaked at 925° F. for 2 hr.; quenched and aged in boiling water for 2 hr.

The alloy containing 2.5 per cent. copper, 0.5 per cent. magnesium, 1.25 per cent. iron, and 0.25 per cent. silicon has, as sand cast, an ultimate strength of about 25,000 lb. per sq. in., an elongation of about 5 per cent., and a Brinell hardness of about 60. These properties, by a short heat treatment involving heating at 950° F. for 2 hr., quenching in boiling water, and aging for 2 hr., either in this boiling water or at 300° F., are altered to an ultimate strength of about 29,000 lb. per sq. in., an elongation of about 3.5 per cent., and a Brinell hardness of about 67.

The effect of increasing the copper content from 2 to 4 per cent., when that of magnesium, iron, and of silicon is kept constant at 0.45, 1.25, and 0.25 per cent., respectively, is to decrease the percentage of elongation more in proportion than to increase the ultimate strength, whether the low-copper duralumin be in the sand-cast or in the heat-treated condition (Table 12).

Magnesium evidently has a greater influence on the mechanical properties than copper. Comparison of the 2 per cent. copper alloys with magnesium content at 0.25 and at 0.50 per cent., respectively, shows that the ultimate strength and percentage of elongation were perceptibly altered by heat treatment only in the latter alloy. The effect of magnesium in excess of 0.5 per cent. in the alloys containing between 2.25 and 2.75 per cent. of copper has not yet been determined.

The low-copper duralumin is particularly well adapted to short heat treatments, for most of the $CuAl_2$ compound and the Mg_2Si are in a finely divided filigree, probably as a ternary eutectic with the aluminum-rich

TABLE 12.—*Physical Properties of Sand-cast Al-Cu-Mg Alloys with Low Copper*

Heat Treatment	Tested after Heat Treatment											
	Immediately		1 Day		2 Days				7 Days		34 Day	
	Ultimate Strength, Lb. per Sq. In.	Elongation, Per Cent.	Ultimate Strength, Lb. per Sq. In.	Elongation, Per Cent.	Ultimate Strength, Lb. per Sq. In.	Elongation, Per Cent.	Ultimate Strength, Lb. per Sq. In.	Elongation, Per Cent.	Ultimate Strength, Lb. per Sq. In.	Elongation, Per Cent.	Ultimate Strength, Lb. per Sq. In.	Elongation, Per Cent.
Copper 2.5 per cent., iron 1.25 per cent., magnesium 0.5 per cent., silicon 0.25 per cent.												
None (as cast)			25,090	4.0			23,500[a]	5.0				
925-2BW2	28,200	6.5	27,920	5.2	28,920	5.9			28,730	6.2	30,860	5.6
925-2CW300-2			29,300	4.5								
925-2CW300-5			30,000	3.8								
925-2CW300-20	31,380	3.0										
925-¼CWBW2					28,630	5.0	21,670[a]	6.2				
925-2CWBW2					27,980	4.8	23,400[a]	5.5				
925-5CWBW2					26,650	4.8	23,300[a]	7.0				
925-5CW												
925-24CW	23,480	4.7										
925-24F	17,930	5.5										
925-96CW300-8									28,950	5.0		
Copper 3.0 per cent., iron 1.25 per cent., magnesium 0.4 per cent., silicon 0.25 per cent.												
None (as cast)			25,770	2.9								
925-2BW2	25,400	3.3	26,610	4.1					27,650	4.4		
925-2CW300-20	33,350	1.0			34,800	2.2						
940-⅜BW-16[b]					27,460	1.5						
(Other Alloys; Heat Treatment 925-5BW2)												
Alloy	As Cast		1 Day		15 Days				554 Days			
Cu 2.08, Mg. 0.41, Si 0.28, Fe 1.18	24,080	6.5	26,370	4.5	27,830	5.7			30,210	4.0		
Cu 3.04, Mg. 0.38, Si 0.26, Fe 1.18	25,280	3.0	27,010	3.5	27,410	2.8			28,850	2.1		
Cu 3.96, Mg 0.40, Si0 24, Fe 1.12	23,830	1.5	30,460	2.5	29,600	2.5			32,030	1.7		

[a] These figures are for Cu 2.17 per cent., Fe 1.55 per cent., Mg 0.25 per cent., Si 0.25 per cent.
[b] Soaked at 940° F. for 40 min., and quenched and aged in boiling water for 16 hr.

solid solution; and the small particles of the two compounds enter into solution very rapidly, 2 hr. at 925 to 950°F. being sufficient time for the alloy to attain equilibrium. The iron is present principally as insoluble sheaves of $FeAl_3$.

Acknowledgment is gratefully made to Mr. Clifford McMahon for his assistance in the experimentation.

DISCUSSION

D. Hanson and M. L. V. Gayler, Teddington, England (written discussion).—At the National Physical Laboratory, the writers have made a number of researches on the relation between the constitution and mechanical properties of aluminum alloys of various types; the results obtained were in good general agreement with those of the authors. The writers, however, did not think that increasing the copper content of sand-cast low-copper duralumin to 4 per cent. necessarily caused a drop in the elongation to 1.5 per cent., as stated on page 872. In the case of sand-cast copper-aluminium alloys they had obtained much greater elongation, in some cases as great as 13 per cent. in heat-treated castings. For example, in a sand casting containing 3.5 per cent. of copper, a strength of 12 tons per square inch and an elongation of 13 per cent. were obtained; in a casting containing 4.5 per cent. copper, a tensile strength of 13 tons, and an elongation of 9 per cent. were obtained. These values were the maximum; the elongation varied considerably, being as low as 5 per cent. in some cases. In the writers' opinion, such variations are due more to unsoundness in the sand casting than to any other cause.

The authors' alloy containing copper 2.5 per cent., magnesium 0.5 per cent., iron 1.25 per cent., silicon 0.25 per cent., which gave the best combination of strength and ductility, is interesting because, according to the writers' experiments, the amount of copper and Mg_2Si present in such an alloy corresponds closely to the limit of solid solubility at high temperatures.

According to their experiments,[7] the limits of solid solubility are reached with a composition of 2 per cent. copper, 0.56 per cent. magnesium, and 0.3 per cent. silicon; the iron content may be ignored as it has relatively little effect on the solubility of the important constituents copper and magnesium silicide.

The writers agree with the suggestion that the physical properties are highly dependent on the composition of the alloys, quenching temperature, time at the quenching temperature, aging temperature, and time at the aging temperature, and their work on the constitution and mechanical properties of aluminum alloys completely confirms this view.

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[7] M. L. V. Gayler: Alloys of Aluminium with Copper, Magnesium and Silicon. *Jnl.* Inst.Met. (1922) **28**, 218.

The quenching temperature is determined by the composition of the alloy, as the maximum hardness and tensile strength depend on the relative amounts of Mg_2Si and $CuAl_2$ that can be held in solid solution at high and low temperatures, respectively.

The writers have shown in the case of the alloys of aluminum with copper,[8] with magnesium and silicon,[9] and with copper, magnesium and silicon,[10] that the amount of age hardening of quenched alloys depends directly on the amount of Mg_2Si and $CuAl_2$ that is retained in solution at the quenching temperature, and that the greatest aging effect is obtained by quenching from that temperature which produces a solid solution most supersaturated with respect to these constituents.

The time at the quenching temperature, consequently, has a marked effect, for there is a definite period that must elapse before equilibrium is obtained and the solid solution becomes saturated at that temperature. According to the size of the casting and the coarseness of the structure, this is a matter of hours or days. The finer the structure of the casting, the less time is necessary for equilibrium to be attained.

The aging temperature and time of aging depend entirely on the composition of the alloy and must be determined specifically for each alloy, though a temperature can be determined that is roughly suitable for many alloys. The time of aging has a marked effect both on the tensile strength and the ductility.

For each alloy there is an optimum aging temperature and an optimum time of aging at that temperature. If the time at this temperature is too prolonged, an increase of strength may be obtained but the ductility will be reduced.

In this respect their experience confirms that of the authors. In the case of duralumin,[11] the writers found that the material definitely deteriorated at 167° C. on prolonged annealing. At 200° C., the critical aging period is less than 1 hr., and after 2 hr. at this temperature the elongation is seriously reduced.

Annealing for 8 hr. at 200° C. reduced the elongation from 25 per cent. (as aged at room temperature) to 6 per cent., while the strength increased from 26 to 30 tons per sq. in. These tests were made on rolled material, but the results agree qualitatively with those obtained by the authors on cast material.

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[8] D. Hanson and M. L. V. Gayler: Heat Treatment and Mechanical Properties of Alloys of Aluminium with Small Percentages of Copper. *Jnl.* Inst. Met. (1923) **29**, 495.

[9] D. Hanson and M. L. V. Gayler: Constitution and Age Hardening of Alloys of Aluminium with Magnesium and Silicon. *Jnl.* Inst. Met. (1921) **26**, 343.

[10] M. L. V. Gayler: Alloys of Aluminium with Copper, Magnesium and Silicon. *Jnl.* Inst. Met. (1922) **28**, 220.

[11] M. L. V. Gayler: Alloys of Aluminium with Copper, Magnesium and Silicon. *Jnl.* Inst. Met. (1922) **28**, 226, 232.

The writers have made prolonged tests on a large number of aluminum alloys, in which specimens were maintained for periods up to eight weeks at various reheating temperatures. The only alloy that appeared to be stable at a temperature of 167° C. was that known as "Y" alloy, which contains 4 per cent. copper, 2 per cent. nickel, and 1½ per cent. magnesium; the hardness was unaffected by annealing for 8 weeks at temperatures up to 167° C. after aging. In their experience, this alloy is the most stable of the high-tensile heat-treated aluminum alloys known.

The writers agree with the authors' views, expressed on page 875, that it is necessary to anneal for a sufficient period and dissolve as much as possible of the compound $CuAl_2$; this is not only necessary in the case of alloys that are subjected to quenching treatment, but may be of great advantage in simple annealing operations. The writers[12] have shown that chill castings containing 4 to 5 per cent. copper can be greatly improved by annealing for two days at 500° C., followed by cooling in air. In their experience, the tensile strength of the chill casting was raised from 10 tons per sq. in. to 15 tons by this treatment, the ductility being, at the same time, appreciably improved.

Finally, the authors will find a complete account of the constitution of alloys of the duralumin type in the published works of the present writers. They there show that the compounds Mg_2Si and $CuAl_2$ are of the greatest importance in connection with the heat treatment of duralumin and similar alloys. The effects of these compounds have been studied individually and collectively. One of the writers has determined the constitution of the quaternary system aluminium-copper-magnesium-silicon[13] over a sufficiently wide range of composition and temperature to enable the behavior of duralumin on quenching to be understood, and has shown that the aging process depends on both the compounds Mg_2Si and $CuAl_2$. In so far as aging at room temperature is concerned, this effect is due largely to Mg_2Si; to this extent the authors' conclusion, on page 883, is correct. The effect of $CuAl_2$ on aging at room temperature is smaller, but with prolonged annealing at higher temperatures this effect becomes considerable. The authors will also find in the account of this work the effects of excess of magnesium and copper on the constitution, age-hardening and mechanical tests of alloys of this type.

SAMUEL DANIELS (authors' reply to discussion).—It has been questioned whether an increase in copper content caused a drop in the per-

[12] D. Hanson and M. L. V. Gayler: The Heat Treatment and Mechanical Properties of Alloys of Aluminium with Small Percentages of Copper. *Jnl.* Inst. Met. (1923) **29**, 491.

[13] M. L. V. Gayler: The Constitution and Age-hardening of the Quaternary Alloys of Aluminium, Copper, Magnesium and Magnesium-silicide. *Jnl.* Inst. Met. (1923) **30**, 139.

centage of elongation; our reference was to the sand-cast and not to the heat-treated material. The authors are pleased to learn that the experimentation at the National Physical Laboratory, with which they are familiar, was independently corroborated by their practical work on the heat treatment of the sand-cast alloys.

Scratch and Brinell Hardness of Severely Cold-rolled Metals

By M. F. Fogler,* Ph D., and E. J. Quinn,† Chicago, Ill.

(New York Meeting, February, 1925)

In a recent paper, Rawdon and Mutchler[1] gave some exceptionally interesting results on the Brinell and scratch hardness of severely cold-worked metals. In their work, they found that, on continued cold rolling, the metal hardened up to a particular point and then reversed and became softer; this was true for both Brinell and scratch hardness values. The generally reported behavior[2] of metals, with respect to Brinell tests on cold-worked material, is that the metals harden up to a certain point and then, on further cold rolling, no change in Brinell hardness occurs. Jeffries and Archer[3] state that there is little difference between the scratch hardness of annealed and cold-worked metals; the work of Faust and Tammann[4] also indicated no difference between the hardness of annealed and cold-worked copper.

Rawdon and Mutchler found, when they plotted the reduction ratio (initial thickness divided by thickness after rolling) against the hardness value for the cold-rolled material, that the hardness number increased up to a reduction ratio of about 3 and then decreased and became even smaller than that for the annealed metal. This behavior was reported for both scratch and Brinell hardness; Figs. 1 and 2 show their results for Brinell hardness on the metals for which they published data. This is an exceptionally interesting phenomenon, if it occurs under all conditions of rolling, and would have an important bearing on the practice of cold

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[1] Henry S. Rawdon and Willard H. Mutchler: Effect of Severe Cold Working on Scratch and Brinell Hardness. *Trans.* (1924) **70**, 342.

[2] A. Portevin: La dureté à la bille du cuivre et des laitons écrouis. *Rev. de Met.* (1919) **16**, 235.

[3] Zay Jeffries and Robert S. Archer: The Properties of Cold-worked Metals. *Chem. & Met. Eng.* (1922) **27**, 882.

[4] Faust and Tammann: *Ztschr. Physik. Chem.* (1910) **75**, 108.

rolling. We made an attempt to duplicate Rawdon's results but have not been able to do so; the present paper records the results of our experiments.[5]

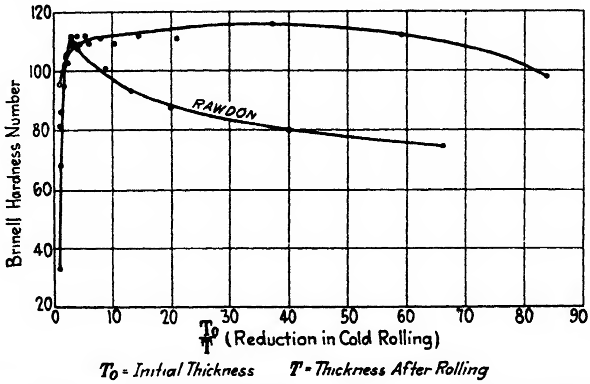

FIG. 1.—EFFECT OF SEVERE COLD ROLLING ON HARDNESS OF COMMERCIAL COPPER.

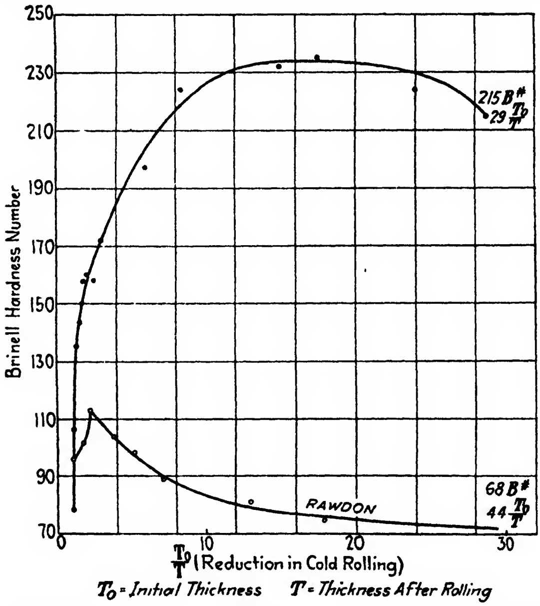

FIG. 2.—EFFECT OF SEVERE COLD ROLLING ON HARDNESS OF LOW-CARBON INGOT IRON.

COPPER EXPERIMENTS

Brinell Hardness

A bar of half hard commercial copper 1 by 1⅛ by 12 in. was annealed at 450° C. for 1 hr. and allowed to cool in the furnace for 15 hr.; the temper-

[5] Since this paper was written, Mr. H. Moore in a paper presented before the fall meeting of the Institute of Metals in England, confirmed our conclusions as regards to the behavior of metals on cold rolling.

ature at the time the bar was removed was 175° C. This treatment insures thorough annealing. A sample was cut off for the determination of the Brinell number of the annealed sample. As the bar was badly coated with oxide, the problem of removing this oxide without changing the hardness of the sample arose. The surface was prepared for Brinell impressions in four ways: (1) It was cleaned with nitric acid; (2) it was ground down with No. 1 emery paper; (3) it was lightly ground down with emery and polished; (4) it was ground down with from No. 1 to No. 0000 emery paper and highly polished with alumina. Table 1 gives the results from ten impressions on the various surfaces. A load of 5 kg. was used on the 1/16-in. ball for 30 sec. These results, which show a difference of over seven Brinell numbers, depending on the manner of surfacing, indicate that care must be taken in preparing a surface for Brinell tests. They show that the surfaces that are least worked give the lowest Brinell number. It seems that acid or a light polish are the best for preparing surfaces, as they give the lowest Brinell number for annealed material.

The remainder of the bar was rolled on water-cooled rolls. Samples were cut off at each second or third pass for hardness tests. The bar was cooled in water after each pass, in order to prevent the temperature from rising to the point where annealing takes place. Twenty-two samples were taken for hardness tests.

TABLE 1.—*Brinell Hardness of Annealed Copper Bar*

Surface Cleaned with HNO_3		Surface Ground Down with No. 1 Emery Paper		Surface Ground Down Lightly and Polished		Surface Ground Down from No. 1–0000 and Highly Polished	
Diameter of Impression, Mm.	Brinell No.	Diameter of Impression, Mm.	Brinell No.	Diameter of Impression, Mm.	Brinell No.	Diameter of Impression, Mm.	Brinell No.
0.42	35.1	0.40	38.5	0.42	35.1	0.42	35.1
0.43	33.4	0.39	40.9	0.43	33.4	0.42	35.1
0.44	31.8	0.38	43.3	0.43	33.4	0.42	35.1
0.43	33.4	0.38	43.3	0.425	34.2	0.42	35.1
0.44	31.8	0.39	40.9	0.43	33.4	0.42	35.1
0.43	33.4	0.39	40.9	0.42	35.1	0.41	36.9
0.43	33.4	0.39	40.9	0.43	33.4	0.43	33.4
0.43	33.4	0.40	38.5	0.42	35.1	0.41	36.9
0.43	33.4	0.38	43.3	0.41	36.9	0.42	35.1
0.44	31.8	0.40	38.5	0.41	36.9	0.42	35.1
Average.......	33.1		40.9		34.8		35.3

The Brinell numbers were determined on a Micro-Brinell machine with a 1/16-in. ball and 5-kg. load. The impressions were measured at

100 diameters and the results were given in Table 2; they are plotted in Fig. 1. The value $\frac{T_0}{T}$ is the reduction ratio, where T_0 is the initial thickness and T the thickness after rolling.

TABLE 2.—*Brinell Hardness of Cold-rolled Copper Bar*

No.	Thickness, Inches	Reduction, Inches	Diameter of Impression, Mm.				Average Diameter Mm.	Brinell Number	Reduction Ratio, $\frac{T_0}{T}$
1	1.003		0.43	0.43	0.43	0.43	0.430	33.4	1.0
2	0.819	0.184	0.27	0.28	0.28	0.28	0.277	81.7	1.22
3	0.729	0.090	0.26	0.27	0.27	0.26	0.265	87.2	1.38
4	0.626	0.103	0.26	0.25	0.25	0.26	0.255	95.5	1.60
5	0.543	0.083	0.25	0.25	0.25	0.24	0.247	102.8	1.85
6	0.470	0.073	0.24	0.25	0.24	0.25	0.245	104.7	2.14
7	0.403	0.067	0.25	0.25	0.24	0.25	0.247	102.8	2.49
8	0.337	0.066	0.25	0.24	0.24	0.23	0.240	109.3	2.98
9	0.292	0.045	0.24	0.24	0.24	0.24	0.240	109.3	3.54
10	0.248	0.044	0.24	0.23	0.23	0.24	0.235	112.0	4.04
11	0.216	0.032	0.24	0.24	0.24	0.24	0.240	109.3	4.65
12	0.197	0.019	0.24	0.23	0.24	0.23	0.235	112.0	5.10
13	0.164	0.033	0.24	0.24	0.24	0.24	0.240	109.3	6.12
14	0.125	0.039	0.24	0.23	0.24	0.24	0.237	111.0	8.00
15	0.096	0.029	0.24	0.24	0.24	0.24	0.240	109.3	10.50
16	0.069	0.027	0.24	0.23	0.23	0.24	0.235	112.0	14.50
17	0.044	0.025	0.24	0.23	0.23	0.23	0.232	111.0	22.8
18	0.027	0.017	0.23	0.23	0.23	0.24	0.232	116.0	37.2
19	0.017	0.010	0.24	0.24	0.23	0.23	0.235	112.0	59.0
20	0.012	0.005	0.24	0.26	0.26	0.25	0.252	98.5	83.5
21	0.009	0.003	0.26	0.24	0.24	0.26	0.250	100.3	111.0
22	0.008	0.001	0.26	0.25	0.25	0.25	0.252	98.5	125.0

Scratch Hardness

The scratch hardness of these samples was taken on a machine essentially like that described by Hankins.[6] The results for scratch hardness in the direction of the rolling are given in Table 3; a load of 100 gm. was used. Cross scratch hardness showed no consistent difference.

[6] G. A. Hankins: Relation Between Width of Scratch and Load on Diamond in Scratch Hardness Test. *Engineering* (1923) **115**, 537.

TABLE 3.—*Scratch Hardness of Cold-rolled Copper*

No.	Width of Scratch, ×500		Average, ×500	Width, Mm.	No.	Width of Scratch, ×500		Average, ×500	Width, Mm.
1	8	8	8.0	0.016	12	7	6	6.5	0.013
2	8	7	7.5	0.015	13	7	6	6.5	0.013
3	6	7	6.5	0.013	14	6	7	6.5	0.013
4	6	7	6.5	0.013	15	6	6	6.0	0.012
5	7	6	6.5	0.013	16	6	6	6.0	0.014
6	6	7	6.5	0.013	17	7	7	7.0	0.012
7	6	6	6.0	0.012	18	6	6	6.0	0.012
8	6	6	6.0	0.012	19	7	7	7.0	0.014
9	6	6	6.0	0.012	20	6	6	6.0	0.012
10	6	6	6.0	0.012	21	6	6	6.0	0.012
11	6	6	6.0	0.012	22	6	6	6.0	0.012

IRON EXPERIMENTS

A low-carbon ingot iron bar 0.4 in. by 1 by 12 in. was annealed at 800° C. for 1 hr. and allowed to cool slowly over night. The bar was then worked and sampled in a manner analogous to that for copper. The results are given in Table 4 and plotted in Fig. 2. A load of 15 kg. was used for these Brinell numbers instead of 5 kg.

TABLE 4.—*Brinell Hardness of Cold-rolled Low-carbon Iron*

No.	Thickness, Inches	Reduction, Inches	Diameter of Impression, Mm.				Average Diameter, Mm.	Brinell Number	Reduction Ratio, $\frac{T_0}{T}$
1	0.406		0.52	0.52	0.52	0.52	0.520	68.5	1.0
2	0.386	0.020	0.42	0.42	0.42	0.41	0.417	106.7	1.05
3	0.343	0.043	0.37	0.37	0.37	0.38	0.377	135.3	1.23
4	0.299	0.044	0.36	0.37	0.36	0.36	0.363	143.4	1.35
5	0.275	0.024	0.36	0.35	0.36	0.35	0.355	150.0	1.47
6	0.253	0.022	0.34	0.35	0.35	0.34	0.345	158.3	1.6
7	0.231	0.022	0.34	0.34	0.35	0.35	0.345	158.3	1.75
8	0.199	0.032	0.34	0.34	0.34	0.34	0.343	160.0	2.04
9	0.167	0.032	0.35	0.33	0.35	0.35	0.345	158.3	2.43
10	0.134	0.033	0.33	0.33	0.33	0.33	0.330	172.0	3.00
11	0.100	0.026	0.33	0.32	0.31	0.31	0.317	185.5	4.06
12	0.067	0.033	0.31	0.31	0.30	0.31	0.3075	197.5	6.0
13	0.048	0.019	0.28	0.29	0.30	0.29	0.290	224.0	8.45
14	0.027	0.021	0.29	0.28	0.28	0.29	0.285	232.0	15.0
15	0.023	0.004	0.28	0.28	0.29	0.28	0.2825	235.5	17.5
16	0.020	0.003	0.30	0.28	0.28	0.30	0.290	224.0	20.3
17	0.017	0.003	0.31	0.30	0.30	0.31	0.305	200.0	24.0
18	0.014	0.003	0.30	0.29	0.30	0.29	0.295	215.0	29.0

Discussion of Results

The Brinell results for both copper and iron show an increase in hardness on cold rolling, up to a certain point when the Brinell number becomes constant. The only place where a slight decrease is indicated is in the thinnest samples. A close examination of these samples will show that a sharp Brinell impression is not obtained, but all of the metal in the vicinity gives a little, thus giving a dent rather than a sharply outlined Brinell impression. This tends to give a larger apparent diameter of the impression and thus a lower Brinell number. The data for scratch hardness indicate that on cold work the scratch hardness increases slightly up to a certain point then remains constant, although this increase in hardness is not of the same magnitude as that of the Brinell.

These results indicate that a reversal of hardness, as found by Rawdon and Mutchler, does not occur under all conditions of commercial rolling practice; and in view of the fact that previous investigators have not found such a reversal, it seems not improbable that it might be characteristic of the particular rolling conditions prevailing in Rawdon and Mutchler's experiments. It should be noted that the Brinell hardness given for annealed copper by Rawdon was much higher than that usually given, even with a load of 500 kg. on a 10-mm. ball and is very much higher than the value we find. Doctor Rawdon[7] has suggested that the difference between our results and his may be due to a difference of rate of deformation.

Our thanks are due to Mr. R. S. Dean under whose general supervision this work was carried out.

DISCUSSION

H. S. Rawdon,* Washington, D. C.—We had the privilege of looking over the data just given before they were published and we were not able to suggest any convincing reason for the differences that were secured here as compared with those that were reported by us a year ago. However, in the meantime (*i. e.*, since the presentation a year ago), we have done considerable work along the same line and have not secured results that would lead us to change the conclusions that we reached and reported. The only suggestion that I would offer is that the rate or mode of deformation probably has something to do with the results that are obtained in work of this kind. Theoretically, there should be no reason for belief that a metal will continue to harden indefinitely as it is rolled thinner and thinner. As the metal becomes very thin, it approaches the structure of a single crystal, as has been shown by *x*-

* Physicist, Bureau of Standards.

[7] Personal communication.

ray studies of the crystal structure, and we have every reason to believe that the hardness of a single crystal is not so great as the hardness of the aggregate of crystals of the same material.

Recently we had an experience that strengthened our belief that the rate and method of rolling do affect the properties obtained in the thin-rolled stock. I am not at liberty to describe the method used in making this material. This metal (a roll of thin strip steel 2 in. wide, several feet long, and less than 0.003 in. thick, was exhibited by the speaker) was rolled, without any annealing whatever, from a thickness of 0.080 in. to less than 0.003 in. This metal will withstand quite severe deformation. Bending it back and forth shows that there is considerable ductility even after it has been rolled down to 0.003 in. It is not at all like hard-rolled strip steel, but will withstand being hammered flat upon itself and has every indication of being "softer" than ordinary cold-rolled steel of the same thickness.

Carl Benedicks,* Stockholm, Sweden.—Is there any difference as to the time factor? If in the determinations carried out by Rawdon a considerably longer time is used, probably the severely reduced metal can adapt itself more slowly under the stress of the Brinell test than if the time alone is shorter. We know very little about any considerable influence of the time factor, but it seems to be an item that might have some influence on this problem.

H. S. Rawdon.—The question of time was considered in the work, particularly with some of the softer metals, and we made the test of hardness in those cases directly after rolling. We also made it on the same material after it had stood for a week or so, but we did not get differences that seemed to be significant. In the case of copper and iron, the tests were made a few days or a week after rolling.

M. F. Fogler,† Chicago, Ill.—In the case of the copper, we measured the Brinell number as soon after the rolling as possible and also several months later, and we found no change in the Brinell number over that length of time.

Alvin L. Davis,‡ Waterbury, Conn.—In the case of the metals reported on a year ago, were not the reductions very much less individually than in the case of those reported to us this morning? Were there not, perhaps, ten passes through the rolls to perform what was done in one or two in the more recent work?

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* Director, Metallographic Institute of Stockholm.

† Metallurgical Engineer, Western Electric Co.

‡ Director of Research, Scovill Mfg. Co.

H. S. Rawdon.—The work was on an entirely different scale. The work we did was on small specimens with hand rolls; this recent work was on a larger scale, using good-sized commercial rolls. I have not compared them as to the exact reductions per pass, but I think our reductions were considerably less than those shown in this later work.

Redistillation of Zinc

By Kurt Stock,* Fish Creek, Wis.

(New York Meeting, February, 1925)

The grades of spelter demanded by the consuming industries were not definitely established until the American Society for Testing Materials undertook to fix specifications, based on the varying percentages of the common impurities (lead, iron, and cadmium) as follows:

	Lead, Per Cent.	Iron, Per Cent.	Cadmium, Per Cent.	Total, Not Over. Per Cent.
A. High grade	0.07	0.03	0.05	0.10
B. Intermediate	0.20	0.03	0.50	0.50
C. Brass special	0.75	0.04	0.75	1.20
D. Prime western	1.50	0.08		

The question which grade was the best for certain purposes and why was left unanswered. The conservatism of the zinc-smelting industry and the unwillingness of the spelter-consuming industries to engage in research work prevented the full benefits being obtained that such standardization promised. The custom smelters, producing spelter in pigs or plates, found it impossible to adhere closely to the established limits on account of the variety of ores treated; and the smelters with long-established and known brands, or those manufacturing their metal into marketable products, like sheet zinc, did not have to abide by the newly established grades based on chemical percentages.

Smelters engaged in the smelting of custom ores had occasional complaints about the quality of their metal, as some of the consumers, especially brassmakers and some galvanizers, used the rigid standards of the A. S. T. M. as a basis for obtaining redress from zinc smelters whenever some of their work was faulty. Indirectly, much good resulted from such complaints; for while the brassmakers and galvanizers, on the whole, did not know what was wrong, the metallurgists in charge of zinc smelters were induced to abandon their conservatism and study the influence of impurities in spelter from the point of view of the consumer. For some of us, spelter gradually ceased to be considered merely spelter; it

* Formerly Superintendent, Bartlesville Zinc Co., Bartlesville, Okla.

was recognized as an alloy of zinc, lead, iron, and cadmium. More attention was paid to the mixing of ores, to obtain metal of a certain composition, and valuable, although sometimes quite perplexing, results were frequently reached.

The greatest impetus to this study was given by the war, when the demand for brass for munitions reached unprecedented dimensions and the bidding and counterbidding for high-grade zinc, which was not in existence, caused the price of this grade to soar. Smelting companies that had not relied on the fame of their brand and had been forced to investigate the qualities of their changing spelter, resulting from constantly changing ores, were in a commanding position and ready to go ahead in proving the results of their research work. The Bartlesville Zinc Co., of the American Metal Co., was in such a position, and was the first to enter the field of producing highest grade zinc from common and impure ores. Electrolytic zinc, at that time, was in its infancy and of little consequence.

It will lead us too far afield to describe here the many proposals for controlling the impurities that enter the spelter in the smelting process but we must mention why and how spelter is thus contaminated.

Spelter Impurities

Lead

Any zinc blende carrying 3 per cent. of lead will yield a metal of the prime western quality; even the first draw will not reach the quality of brass special. An increase in the lead content of the ore, say not more than 8 or 9 per cent., will only slightly raise the lead content of the spelter, and never in the proportion of the increase of lead in the ore.

Carbonate ores behave in the same manner, only generally the lead will be found to distill more freely than in roasted zinc blende. Zinc silicate ores are of little consequence to the custom smelter and need not be discussed here.

Lead is actually volatilized and condensed, although its boiling temperature lies between 1450° and 1600° or 1800° C., according to different authorities; *i. e.*, considerably beyond any temperatures reached inside the zinc retorts. The fact that with most leady zinc ores the percentage of the lead in the spelter is lowest in the first draw, and increases with the succeeding draws, seems sufficient proof that the smelting temperature controls this impurity. However, in his search for pure ores, the author has several times found a concentration of lead in the first draw, and has obtained a second-draw metal of greatly better quality. Such contradictory results point to the fact that the physical conditions of the lead and zinc in the ore have a greater influence on rates of recovery during the distillation process than is commonly realized.

Iron

Iron enters the distilled metal from two sources: contact of the spelter with iron tools and molds, which are the more readily attacked the hotter the spelter is; and solution of reduced (metallic) iron, contained in the charge, by the zinc standing in the condenser. The type of condenser commonly used in America is to blame for this unnecessary contamination as the molten zinc in the condenser rests against the ore charge and causes an intimate mixing, whenever the metal drawer removes the zinc by means of the well-known "scratching." In European practice, the condenser is formed with a clay bridge at the back, which separates the distilled zinc from the ore charge; but this condenser requires more careful furnace work in its setting up and loaming, and is a little more inconvenient in drawing metal. Iron can be kept out of spelter almost entirely, if the precautions are taken that suggest themselves to the zinc metallurgist from this description of the causes of its presence.

Cadmium

A few zinc mines produce ores practically free from cadmium, but most of the ores available to the custom smelter carry this impurity in varying proportions, generally less than 0.2 per cent. Cadmium behaves very much like zinc and distills freely. Its boiling point (given by different authorities at from 720° to 860° C.) and the boiling point of zinc (given at from 890° to 1040° C.) are too close together to allow an even approximately quantitative separation in the distilling process.

Schnabel states "when zinc blende is roasted, a great part of its cadmium content is lost by volatilization. Thus a blende from Silesia contained 0.11 per cent. of cadmium before roasting and 0.042 per cent. after." With different types of roasters, different results will be obtained; but any blende will have its cadmium content reduced during the roasting process.

The slow increase in temperature during the retorting process allows advantage to be taken of the difference in the boiling points of cadmium and zinc and leads to a concentration of cadmium in the first-draw metal. The second-draw carries much less cadmium, and the third-draw hardly any. The retort residues, however, retain traces of this metal, showing that a complete elimination of this volatile element is practically impossible under retort smelting conditions.

Many proposals have been made for the removal of cadmium from zinc ores before roasting, during roasting, and before smelting, but they are all uneconomical or impractical, considering the large amounts of zinc, so very similar in its reactions, in the presence of such minute quantities of cadmium as are found in the average zinc ore.

Analyses of Spelter

Some characteristic analyses of the several grades of spelter produced from different ores may prove interesting; only average figures are submitted.

	Lead, Per Cent.	Iron, Per Cent.	Cadmium, Per Cent.
Montana sulfides, concentrates	3.32	3.02	0.170
First-draw spelter	0.76	0.012	0.105
Second-draw spelter	1.65	0.022	0.041
Third-draw spelter	2.76	0.046	0.020
Colorado sulfides, concentrates			0.163
Colorado, carbonates, crude			0.124
Both ores mixed for smelting and fired very slowly			
First-draw spelter	0.60	0.035	0.560
Second-draw spelter	1.20	0.080	0.200
Third-draw spelter	2.50	0.265	0.090
Australian sulfides, concentrates			0.180
First-draw spelter	1.15	0.011	0.179
Second-draw spelter	1.92	0.024	0.070
Third-draw spelter	2.50	0.103	0.027
Arizona sulfides, concentrates } roasted mixed. Mexican sulfides, concentrates }			0.171
First-draw spelter	0.920	0.020	0.220
Second-draw spelter	1.515	0.046	0.083
Third-draw spelter	2.74	0.100	0.059

In the practice of the Mid-Continent zinc smelters, the three draws represent approximately the following percentages of the metal produced: First-draw, 36 to 38 per cent.; second-draw, 50 to 55 per cent.; third-draw, 9 to 12 per cent.

Spelter Redistillation

When deciding on the best, quickest, and cheapest method of producing high-grade spelter in large quantities from custom ores, which the Bartlesville Zinc Co. was obliged to smelt under its contracts, the method of redistilling common spelter was tried. At different times and places, redistilling has been practiced, but always on a small scale and nearly always to recover zinc from scrap alloys. We believed that the redistillation of virgin spelter would be a much simpler operation, so the company constructed four full-size, double furnace blocks at Bartlesville, later trebling this capacity by erecting like furnaces at its other Oklahoma plants. Preliminary tests were made in December, 1914, and by January, 1915, detailed plans were ready for execution.

The redistilling plant was located on a level piece of ground between the main smelter and the Lanyon-Starr branch, and a considerable distance from the furnaces and other buildings of either smelter. The

refining furnaces were housed in the type of building usual in the Mid-Continent gas field, but more room was provided all around the furnaces, to obtain better ventilation and greater convenience in working. The buildings, Fig. 1, were arranged end to end, with fan house and retort

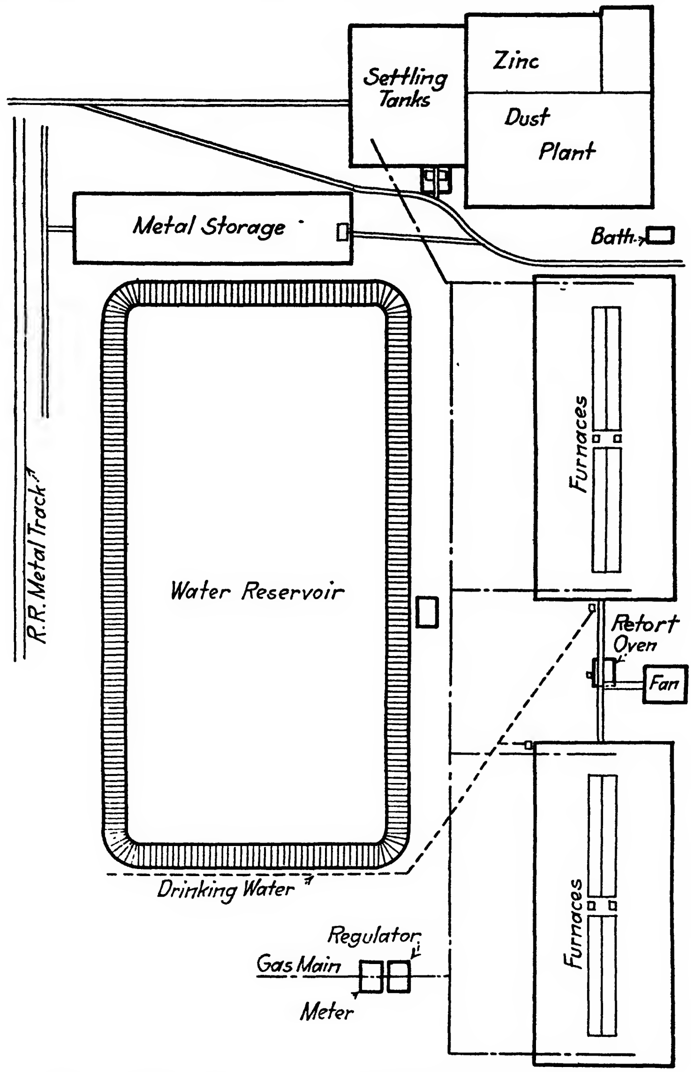

Fig. 1.—Redistilling plant of Bartlesville Zinc Co.

temper oven between them; each building contained two blocks of furnaces, also end to end. The stacks were between the blocks, each stack serving two furnaces, being divided vertically by a baffle wall about 20 ft. high. The settling tanks and the metal storage house were to one

side, joined to the furnaces by industrial tracks. Railroad loading platforms were at the far end of the storage house.

The regular crew of men consisted of: 1 foreman; 6 firemen, in 8-hr. shifts; 24 metal drawers, in 8-hr. shifts; 16 chargers and retort changers; 2 men breaking sticks and loading charge trucks; 1 man cleaning up and painting spelter molds. During hot weather, quite a few extra men were required and the labor turnover was enormous, especially during 1915 and 1916. Later, these conditions improved somewhat.

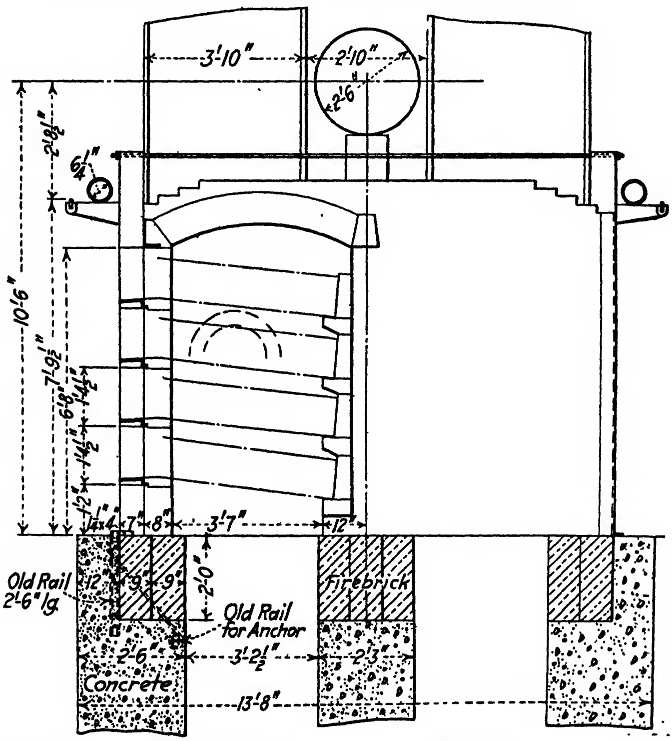

FIG. 2.—CROSS-SECTION OF REFINING FURNACE AT BARTLESVILLE ZINC CO.

All material needed by the refinery, like green retorts, condensers, fireclay, coke and coal, as well as all products removed from the refinery, as metal, oxides, discarded retorts and condensers, were handled by the regular smelter crews attending to similar work for the ore furnaces.

The type of furnace usual in the natural-gas belt was selected, retorts of extra heavy thickness were made, and condensers with "bridges" at the large end were prepared. The back shelves on which the retorts rest were so located that the pitch of the retorts was opposite to that used in the ore-smelting furnaces. Fig. 2 shows these points clearly.

The ore furnaces of the natural-gas belt are, in effect, merely a double horizontal flue, with retorts placed at right angles to the length of this

flue, the gas (mixed with air under pressure burning in jets among the retorts) finding its way up the arched roof and down the flue to the end of the block, where it escapes at an incandescent heat through short chimneys. The retorts are inclined forward, so as to make charging and discharging of the ore mixed with reduction fuel easier, and to prevent the condensed zinc from running back. In newly built ore furnaces, the back of the retort is from 6 to 8 in. higher than the mouth. The condenser, wide open at both ends, is loamed to the retort by finely ground coking coal, mixed with small amounts of inferior clay. The mouth of the condenser is ordinarily stuffed with a loose moistened mixture of ground coal and screened skimmings or other zinkiferous sweepings or byproducts.

For the redistilling operations, the retorts were of the same outside dimensions as those used in ore smelting, namely 51 in. long by 11 in. in diameter. The inside dimensions were 48 by 8 in., which meant a 3-in.

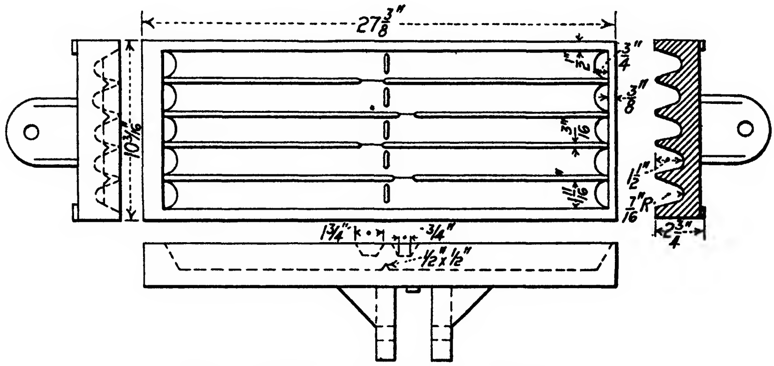

FIG. 3.—CONSTRUCTION OF STICK MOLD.

thickness for the butt and 1½ in. for the side walls. The butt of the retorts was placed 6 in. lower than the mouth and, at that pitch, the capacity for molten metal was about 170 lb. for each retort. Later, it was found that, in spite of extra deep and heavy foundations under the center walls, an appreciable settling had taken place as a result of the back thrust of so many tons of metal, so that the final backward pitch was about 9 in.; the holding capacity for molten metal was thus greatly increased, which proved an advantage. The retorts were tempered and inserted hot, as in the ore practice.

The condensers were provided with a clay bridge, which closed somewhat more than one-half of the opening at the wide end. They were carefully attached to the retort mouth and loamed with fireclay ironed smooth with a hot, half-moon stamper. Contrary to the ore smelting method, where the condensers are removed every 24 hr., the refinery condensers remained undisturbed until they broke or choked up.

The common spelter produced by the ore furnaces and intended for redistillation was not cast into the usual flat molds or pigs, but into sticks, each weighing about 5 lb. A special cast-iron mold, Figs. 3 and 4, was prepared, in which ten sticks were made at one pouring. These sticks were stacked on special charge trucks, Fig. 5, and kept near the ends of the redistilling furnaces for one day, so that they would be entirely dry and would not cause steam explosions when put into the distilling retorts.

The molds, Fig. 6, receiving the redistilled metal were furnished with a small "pouring cup," from which the metal overflowed gently into the

FIG. 4.—STICK MOLD AND SPELTER STICKS.

mold proper and required no skimming. The appearance of the finished zinc was greatly enhanced by this method; the brand was sharp and clear, the top of the plates smooth, beautifully crystallized, without discoloration, and free from inclusions of dust or particles of skimmings. The molds were cleaned daily and painted with a mixture of graphite and kerosene; the zinc did not absorb any iron from the mold whatever.

The refinery furnaces were at first operated by natural draft. Near each gas burner was an air hole which could be adjusted in size to meet the varying requirements of heat. Very soon, however, we installed the usual pressure air system because with every increase in wages the men became more unwilling to attend to the slightly more complicated regulation of a natural-draft furnace.

The method of operating was as follows: Starting with new retorts a "charge scoop" of fine coke (about 5 lb.) was spread over the bottom of

the retort; 150 lb. of zinc, in sticks or slabs, was carefully put in; another scoop of coke added; and the condenser quickly installed, loamed on and

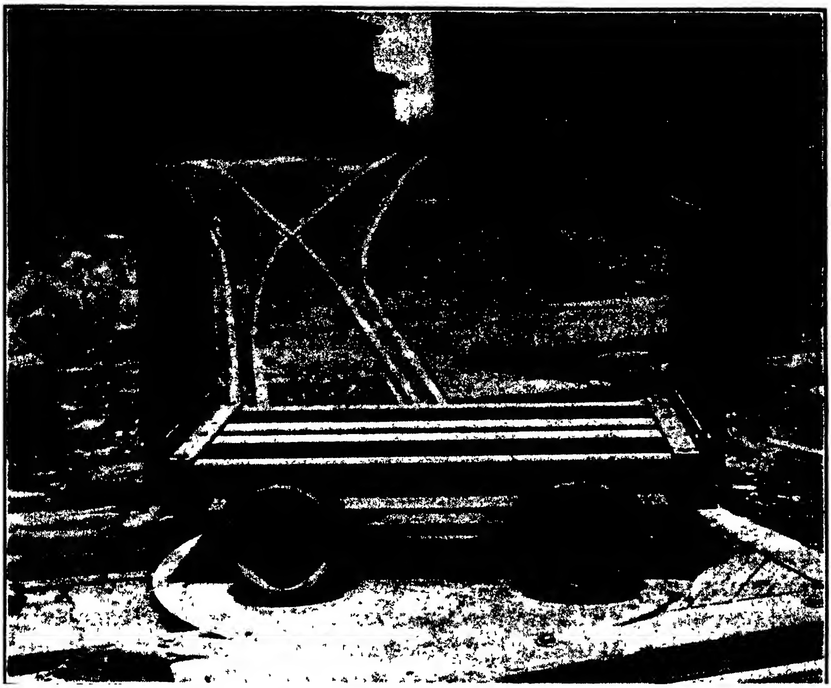

FIG. 5.—HIGH-SIDE CHARGE TRUCK FOR STICK METAL.

stuffed with finely ground semianthracite. As this work proceeded, each charged section was immediately given an increase in gas, so that

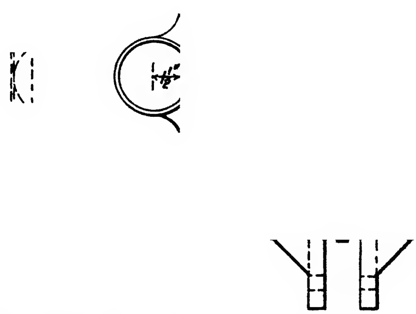

FIG. 6.—SPELTER MOLD WITH POURING CUP.

by the end of charging the chilling caused by the introduction of the cold metal was largely overcome. As soon as distillation began, the firing was reduced and then kept steady for the rest of the 24-hr. period.

The charging of going retorts was accomplished by the use of a special tool, a semicircular trough attached to a curved handle and provided with a stop. The far end of the trough rested on the condenser bridge, the stop against the condenser mouth. A stick of spelter was placed on this charging tool and then pushed into the retort by a second stick; this, in turn, was pushed in by a third, etc., until the required amount was charged. The production of redistilled metal plus the zinc contained in the day's skimmings plus the known furnace loss determined the amount of zinc to be replaced, so that every retort held at all times practically the same amount of crude spelter.

Metal was drawn six times, in 4-hr. intervals, and each draw from each of the eight furnaces was piled separately. Every fourth plate was drilled for samples and, after the results of the chemical analyses were known, the different small piles of spelter were combined, in carload lots, in such a manner that each completed lot held practically uniform material, with only insignificant variations in lead, iron, and cadmium.

Specifications

Previous to this country's entry into the war, specifications for requirements of spelter, especially by the allied nations, varied widely and showed no reference whatever to the grades established by the American Society for Testing Materials. Domestic makers of brass for ammunition purposes required, broadly speaking, spelter with 0.15 per cent. lead and iron combined. France purchased metal on the basis of the following specifications:

Grade	Lead, Per Cent.	Iron, Per Cent.	Cadmium, Per Cent.	Minimum Zinc, Per Cent.
1	0.02	0.02–0.03	0.20	99.75
2	0.38	0.025	0.10	99.50
3	0.20	0.01	0.40	99 40
4	0.30	0.03	0.42	99.25
5	0.70	0.05	0.20–0.25	99.05–99.00
6	1.42	0.08		98.50
Silver Star	0.15	0.03	0.07	99.75

These limits, however, were not always strictly adhered to, either because insufficient tonnage was forthcoming or because it was found that such strict differentiation was not really necessary Frequently, two of the grades were combined, as, for instance, 2 and 4, which allowed the spelter manufacturer sufficient leeway to increase his deliveries. In this combination, the higher lead allowance of grade 2 was combined with the higher cadmium specification of grade 4, and absolute uniformity within these quite sufficiently narrow limits was sacrificed by the buyer.

The English Government purchased practically only two grades, prime western and a 99.9 per cent. zinc plus cadmium quality. The latter specification is of especial interest, as it showed that the "cadmium myth" had no terrors for this government. The most particular customer was the Imperial Russian Government, who bought practically only one grade, 99.9 per cent. pure zinc. Enormous tonnages of this metal were shipped by us, but its production required especial treatment and preparation. The Italian Government adhered generally to the French standards. After its declaration of war, the United States Government published specifications as follows:

Navy Department under Date of June 1, 1917

Grade	Lead, Per Cent.	Iron, Per Cent.	Cadmium, Per Cent.	Minimum Zinc, Per Cent
A	0.07	0.03	0.05	99.85
B	0.20	0.03	0.50	99.35
C	1.00	0.08	0.75	98.00
War Department under Date of July 31, 1917				
A	0.10	0.03	0.50	99.50
B	0.25	0.03	0.50	99.35
C	1.00	0.08	0.75	98.00

Practically none but grade A was demanded; and as the supply proved insufficient the government, in March, 1918, modified its specifications for this grade for both departments to 0.10 to 0.12 per cent. lead, 0.02 per cent. iron, 0.50 per cent. cadmium.

Long before the specifications of the allied governments and the American cartridge brass manufacturers crystallized in the grades just mentioned, redistilling operations of this company were in full swing. The writer had always appreciated the fact that spelter produced from western ores was uneven from day to day, and even in different sections of each furnace on any one day; but these differences were small and it was believed could be controlled to some extent. However, this matter was aggravated by the deterioration in quality of most of the ores, caused by the constantly rising prices of spelter with its great profits to the mines. No ore contracts had provided for such unforseen and unexpected metal prices, or such increase in the cost of mining and smelting, as a result of high wages, high cost of supplies, and general inefficiency of labor. In some cases, adjustments of contract conditions between smelter and mine were made, but not in all. The tendency to "hog" the profits was quite general all around, and its most disastrous first consequence was the output of inferior grades of concentrates, with a constantly declining tenor of zinc, which in extreme cases led to the shipping of enormous tonnages of crude ore. Custom smelters were deluged with

undesirable grades of ore and recoveries began to drop, as there was no time to make the necessary tests for handling such constantly depreciating and changing raw material.

The work of grading the spelter output of the ore furnaces, so as to provide a fairly uniform quality of sticks for redistillation, became more and more difficult, and quickly led to the proper solution of this trouble.

Settling Tanks

Two large settling tanks, Fig. 7, were constructed, the purpose of which was to equalize in quality all crude spelter destined for redistillation. The writer had had experience with the small, coal-fired German type of settling tank, and knew that its inherent drawbacks could be largely overcome. As the lessons of the war demands have taught the consumers of spelter the advantages of uniformity in chemical composition, hereafter more emphasis will be laid upon this point.

Crude spelter is slowly melted under a reducing flame on the high shelf of a pocket-shaped deep tank. The excess lead and iron liquate and collect in the bottom of the tank according to their specific gravities, and a uniform zinc stays on top, which is then tapped off. The amount of iron and lead held in solution in molten zinc, varies with the temperature—just above the melting point of zinc it is saturated with about 0.6 per cent. of lead; when the bath is heated to a point where casting is possible, this content will increase to about 0.9 to 1.1 per cent. As experiment had shown that the lead or iron content of the spelter used in redistillation was of comparatively minor importance, but that uniformity of the metal charged was necessary to the successful output of large quantities of high-grade zinc, these settling tanks fulfilled their purpose admirably.

In small tanks, the floor is usually tamped fireclay and the settled metal is ladled out from a separate well connected by a narrow channel with the main chamber. In these large tanks, the floor was built of several superimposed layers of matched and closely laid firebrick, the top layer forming an inverted arch, safely anchored in the side walls. At the discharge end, a large tile was built in; this was provided with a narrow deep notch, ending in a troughlike projection. The tanks were encased in sheet steel up to the level of the metal bath, preventing outbreaks of metal or leakage through the firebrick; they were provided with heavy rail buckstays all around, as well as on top and bottom. Both tanks were erected on one solid concrete slab and set with the bottom buckstays on a number of parallel rails, permitting the tanks to move freely with expansion or contraction; also air could circulate unhindered beneath the tanks. The products of combustion were removed through small outlets in the arches near the front end, by means of a horizontal flue connecting both tanks. From the middle of this flue rose a short

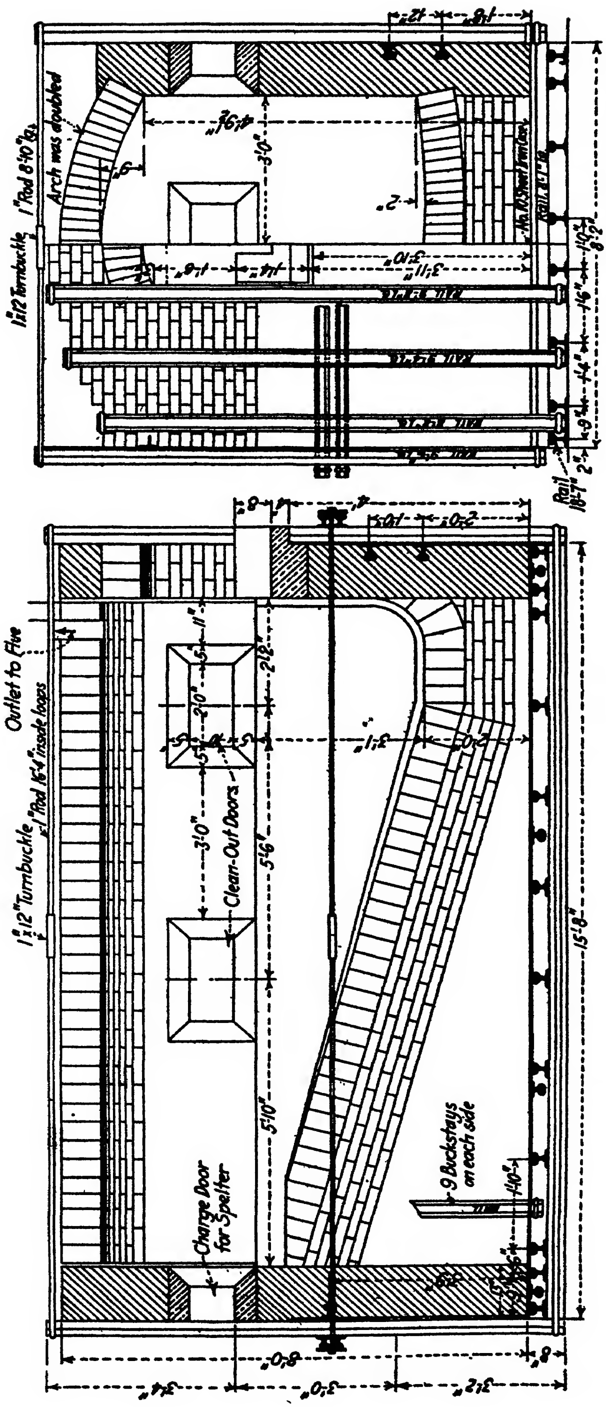

FIG. 7.—SETTLING TANK OF BARTLESVILLE ZINC CO.; NOTE HEAVY TIEING OF BRICKWORK BY RAILS AND RODS ALL AROUND.

stack through the roof of the building. Removable platforms were erected all around and between the two tanks, at a height convenient for all furnace work; about one-third of the tanks were below these platforms, which safeguarded the crew in case the metal should break out below.

To tap, a little of the fireclay filling the notch was scratched off and the molten zinc run into a large, clay-lined ladle, the broad spout of which rested under the trough projection.. The ladle, holding about 500 lb. of

Fig. 8.—Back view of two settling tanks. Trucks with crude spelter intended for treatment on elevated working platform. Two small gas burners are shown, one on each side of charging door. The burners along the sides of the tanks were not used after the first trial. In the center background, the smoke flue connecting both tanks is visible; the short stack was erected in the middle of this flue.

spelter, was suspended from a differential chain hoist, which traveled on a monorail overhead. A row of stick molds was in front of each settling tank, with arrangements for tipping the molds forward and away from the operator's platform. On the other side of the mold stand, and on a lower level, were narrow-gage tracks, on which the spelter trucks, Fig. 5, moved. The cooled sticks were dumped directly on to these trucks, run over a scale, and taken to the redistilling blocks.

The settling tanks were a success in every way; gas consumption was unexpectedly low because of the insulation of the heavy side walls and double arches. The metal bath was skimmed only once in two weeks, and

the skimmings were smelted in the ore furnaces. Lead was removed every 4 to 6 months, depending on the lead content of the crude spelter charged; this lead found a ready market, being pure enough for the trade. The mushy iron-zinc alloy, which separated the lead from the zinc, was removed by means of a large, long-handled, perforated scoop, molded into plates, and refined in the redistilling furnaces, yielding high-quality spelter and a residue of lead and iron that was salable to lead smelters.

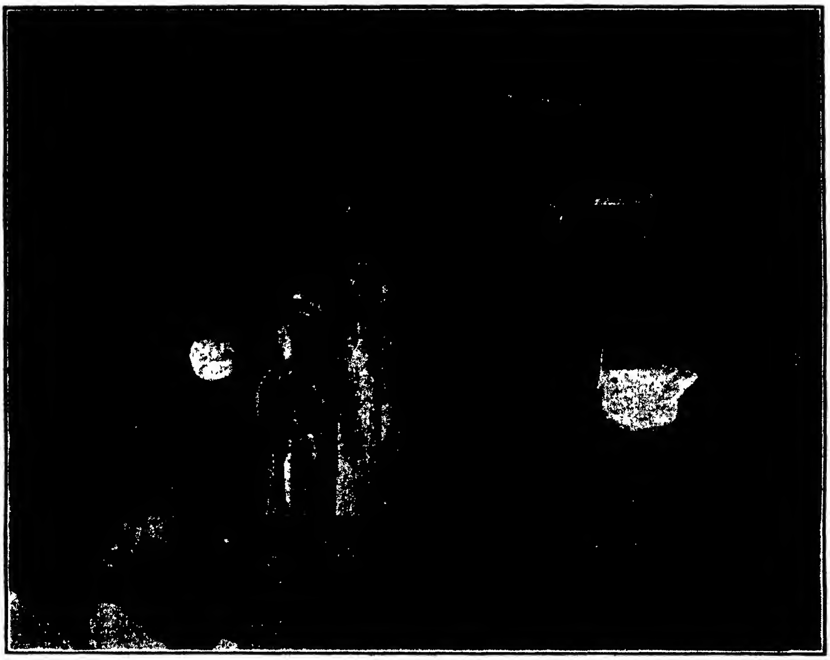

Fig. 9.—Spelter draw car. Refinery furnace showing the central joint stacks, belonging to four furnaces. These stacks had inside baffle walls up to a height of 20 ft., to prevent interference in draft.

The capacity of the tanks was about 1,500,000 lb. of crude spelter per month with a metal loss of 0.4 per cent. One man per 8-hr. shift attended to both tanks, drawing each one every hour, and charging immediately after drawing the same number of plates that were taken out. It was easy and inexpensive to dead-fire the settling tanks, if this was desired for any reason; a sample of zinc removed after a ten days dead-fire, showed the unusually low lead content of 0.500 per cent. Such metal was, of course, too cool for tapping and molding.

As soon as the settling tanks were in operation, the redistilling furnaces produced uniform and reliable metal. Although each one of the six daily draws was a little different in composition, it was like the

corresponding draw of the next day and so on. Typical analyses of that period are as follows:

	Crude Spelter to Tanks	Settled Metal to Refinery	First Draw	Second Draw	Third Draw	Fourth Draw	Fifth Draw	Sixth Draw
Lead, per cent......	2.50	1.000	0.102	0.114	0.125	0.128	0.130	0.130
Iron, per cent.......	0.10	0.033	0.009	0.009	0.008	0.006	0.005	0.007
Cadmium, per cent..	0.06	0.060	0.185	0.115	0.055	0.037	0.013	0.009

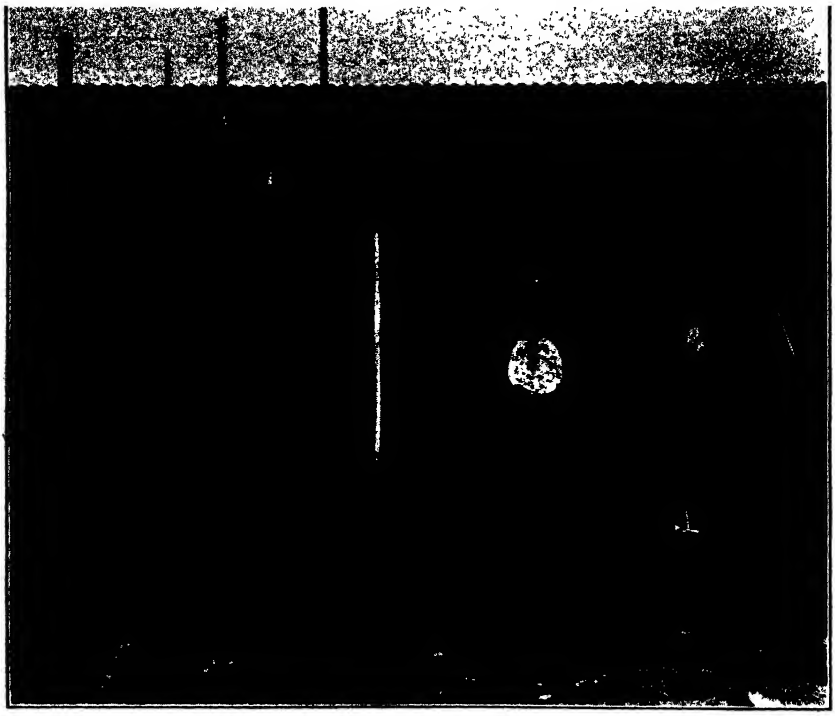

FIG. 10.—A COMPLETE COLLECTION OF REFINERY TOOLS; THE LAST ONE ON THE RIGHT IS THE STICK CHARGING TOOL.

Each draw from each furnace was kept by itself and marked, and the analyses entered into a stock book, from which the carload lots were later determined, so that each shipment was of great uniformity and of absolutely known composition.

Methods of Controlling Cadmium

As the demand for the highest grade, 99.9 per cent. pure zinc, continued to increase and as only occasional draws were of that quality, it was

decided to resort to double redistillation. Lead and iron could be controlled easily; a slow heat in the distillation furnaces yielded spelter of 0.050 per cent. lead and 0.004 per cent. iron, but the cadmium gave trouble. Tests with different temperatures proved that this element could be quickly gotten rid of, if sufficient heat was used, but that it was removed with difficulty if, for the sake of low lead, a low heat was employed. The analyses shown here are typical of such experiments; the crude spelter used was the first draw from high-grade Joplin ores and had not been settled.

Quick, sharp firing:

First draw, per cent. cadmium	0.151 (largely burned off)
Second draw, per cent. cadmium	0.013
Third draw, per cent. cadmium	trace

Slow, moderate firing:

First draw, per cent. cadmium	0.440
Second draw, per cent. cadium	0.381
Third draw, per cent. cadmium	0.231
Fourth draw, per cent. cadmium	0.157
Fifth draw, per cent. cadmium	0.081
Sixth draw, per cent. cadmium	0 035

The control of cadmium was accomplished in two ways: In the first, it was necessary to use a crude spelter low in that element, so stocks of metal, representing the last draw from the ore furnaces, supplemented with the same grade from the company's other plants or purchased from outside smelters were accumulated. This metal, high in lead and iron but low in cadmium, was treated in the settling tanks and there freed from its excess of lead and iron. The product was then subjected to redistillation, with the object of concentrating all cadmium in the first two draws by sharp firing. The next four draws were cast into sticks and used for double redistillation, yielding on the first two draws a metal of 99.9 per cent. zinc plus cadmium quality, and on the other four draws a metal of 99.9 per cent. pure zinc grade.

Representative analyses of double redistillation were:

	Lead, Per Cent.	Iron, Per Cent.	Cadmium, Per Cent.
First and second draws	0.020 to 0.060	0.005	0.070 to 0.120
Third, fourth, and fifth draws	0.040 to 0.050	0.004	0.004 to 0.010
Sixth draw	0.050 to 0.070	0.004	nil to trace

Sixty carloads of 99.9 per cent. pure zinc shipped under one order assayed between the following extreme limits:

Lead, per cent	0.044 to 0.074
Iron, per cent	0.003 to 0.007
Cadmium, per cent	0.006 to 0.021

It should be mentioned that this redistilled metal showed no other impurities whatever, because the ores were singularly free from arsenic and antimony. To avoid these two elements, as well as bismuth, tin, copper, etc., no remelted or scrap metal was purchased for the refinery. The origin of outside third-draw metal was, in all cases, known and was guaranteed by the seller.

The final metallic residue was removed from the retorts every 18 days and was subjected to further redistillation in special retorts, with the object of extracting all remaining zinc. The dross from such final redistillation was separated, according to its origin, into high-lead and high-iron material and sold to lead smelters. Characteristic analyses of such dross residue were:

Zinc, Per Cent.	Iron, Per Cent.	Lead, Per Cent.	Silver, Ounces Per Ton	Gold, Ounces Per Ton
19.25	0.65	79.3	21.66	0.025
28.75	0.55	70.1	17.39	0.010
	44.04	39.85	4.4	0.010

Gallium and indium were found in such dross, which had originated from the redistillation of spelter produced from certain Joplin ores.

In single, as in double, redistillation the metallurgical work improved with practice and recoveries, over a two-year period, were 87 per cent. as marketable spelter; 5 per cent. was the loss by burning and retort absorption; and the skimmings contained the remaining 8 per cent. of zinc in an 80 per cent. product. These latter, called refinery oxides, were handled like high-grade ores and, mixed with only 10 per cent. of dead coal, were smelted in the ore furnaces. The zinc recovery of the refinery oxide charge showed an average figure of 90.94 per cent., in a 42-months continuous run on one ore furnace. All the anthracite stuffing of the refinery condensers had gone into these skimmings, hence the small amount of new reduction fuel. The yield from this charge was an excellent and uniform grade of spelter, somewhere between the intermediate and brass special grades established by the American Society for Testing Materials.

In the operations of the redistilling blocks, the writer was supported by an exceptionally capable foreman who, after the first few months, could be relied on to produce any grade of spelter desired, according to the shipping orders. Regulation of heat, segregation of special draws, mixing into the redistilled metal of weighed amounts of carefully graded and analyzed crude spelter or single redistilled material of off-assay, gave

the operations a latitude unknown in ore-smelting practice, and enabled the plant to turn out huge tonnages of uniform spelter and of any combination of lead, iron, and cadmium demanded. Large melting pots for such mixing of different grades were used for purposes of equalization. An unusual amount of laboratory work was, of course, required and several chemists were kept busy on refinery analyses alone.

Care of Retorts

New retorts yielded, for the first week, a higher grade of spelter than they did later, and advantage was taken of this fact. This was easy to do, as the 18-day cleaning and 36-day changing of retorts were done by sections, proceeding regularly down each furnace in turn. Working costs were kept low under such a system, the work being done strictly on schedule and at great speed. As in ore smelting, the charging and retort-changing crews were allowed to go home as soon as their work was done, so they rarely worked more than 4 hr. For the rest of the time, only one fireman was on duty for each two blocks, and one metal-drawer for each furnace on 8-hr. shifts.

The removal of the dross from retorts to be cleaned or changed was done by the night metal drawer, into special ladles and with special tools, so as to avoid contamination of the redistilled metal with this high-lead and high-iron residue. The amounts so removed were small, as such retorts had not been charged for three days preceding the cleaning-out process, and were worked down low. In the morning, the day crew charged, or changed and charged, these retorts as their first duty, so as to avoid a burning out of the absorbed zinc.

The body of the retorts was deep blue with zinc spinel, and showed stringers of zinc in the fine checks and cracks, so common in clay retorts. The retorts did not break and drop their spelter contents into the furnace; they were closely inspected by the foreman when they were removed from the temper ovens, and discarded if he had the slightest doubt as to their soundness. Small pinholes at times developed after charging; these were readily observable through peep holes in the ends of the furnaces and in line with the spaces between the rows of retorts. Such pinholes were patched with soft clay whenever possible, or were marked for immediate cleaning out and removal, if patching was not possible.

To avoid contamination of the redistilled metal by iron, bronze scratchers were tried, but quickly proved to be unsuitable. Each metal drawer was provided with a large number of the regulation cast-iron scratchers, and was required to use each one only a short time, so that no undue heating of the iron tool could lead to an increase of the remarkably low iron content of the redistilled metal. After the first year's operation, the metal carried never more than 0.005 per cent. iron, with an average

of 0.0035 per cent., which figure is not equalled by any spelter made from pure ores direct, or by any electrolytic zinc.

Producing Modified Grade A by Single Distillation

Early in 1918, after the establishment of more liberal specifications by the United States Government for grade A, and after the Russian demand for 99.9 per cent. pure zinc had ceased, there was a serious decline in price for such grades. Double redistillation with its double operating costs and metal losses became unprofitable, and it was possible to produce the modified grade A by single redistillation from third-draw crude spelter. A very low heat was used, the efficiency of the men and the interest in their work increased, and reliable results were obtained. The tonnage under this treatment decreased considerably, but this was partly offset by the saving of settling costs, decrease in metal losses as a result of longer retort life, simplified handling of the distilled metal, because of great uniformity of the six draws, with the total absence of off-assay lots, etc. The refinery retorts had proved very reliable and, under the conditions of gentle firing, stood up so well that a second cleaning before changing was introduced, thus giving a life of 54 days.

The average analyses of the singly redistilled metal under this method were as follows:

	First Draw	Second Draw	Third and Fourth Draws	Fifth Draw	Sixth Draw
Lead, per cent.	0.050	0.070	0.085	0.090	0.110
Iron, per cent.	0.004	0.004	0.004	0.005	0.005
Cadmium, per cent.	0.200	0.123	0.080	0.040	0.015

Costs

Redistilling costs varied, during the 45 months of continuous operations, from $7 to $10 per ton of crude metal treated, depending largely on tonnage (a factor of slow or fast firing); the average was $8.70. The major items of such costs were as follows: Labor from $5.06 to $6.24 per ton crude spelter. Natural gas was $1.44, based on an average price of 7.9 cents per 1000 cu. ft. at the furnaces. Retort consumption varied from $0.50 to $0.32. Condenser consumption averaged $0.20. Coke (reduction fuel) was $0.01. Semianthracite (for stuffing) averaged $0.21. The balance of the costs comprised repairs to tools and buildings, power, supplies, clay, liability insurance, salaries, water and miscellaneous, all small items.

Tonnage varied from 1600 to 1400 per month, with a gas consumption of 900,000 cu. ft. per day, which included the operation of the settling tanks, retort temper oven, melting pots, etc.

The foregoing description of the process of redistilling spelter shows the remarkable adaptability and latitude in quantity and quality produc-

tion of high-grade zinc, and it will not be surprising to learn that, of all the Mid-Continent smelters practicing redistillation, the Bartlesville Zinc Co. was not only the first to start this process, but the last to discontinue it. Far-reaching economies had gradually been introduced, and the metallurgical work had improved so far, that competition with the old-fashioned brands of high-grade zinc was perfectly possible. The quantity production of electrolytic zinc caused the company to shut down its refineries, thus bringing to a close a most successful emergency process, which will always remain an interesting phase in the history of the metallurgy of zinc.

Other Methods of Refining

For the sake of completeness, there should be mentioned here those other processes of refining zinc in the Mid-Continent field that have come under the author's observation.

Several smelters used a copyrighted process, whereby prime western spelter was freed of its excess lead and iron in a settling tank and charged, in a molten condition, into redistilling retorts through holes in the back end of such retorts in single furnaces. The redistilled metal was dumped into an equalizing tank, and molded out after thorough stirring and mixing. As the charging was done after every draw, and later twice a day, several advantages were obtained. The retorts were kept more uniformly loaded and not exposed to the chilling effect prevailing when charging with stick metal; hence it was easy to keep temperatures at a uniform level, and have draws of equal tonnage. On the other hand, this process failed to take advantage of the control of cadmium by fractional distillation, and therefore never turned out the highest grade of 99.9 per cent. pure zinc.

Another company used graphite pots, similar in design to those used in distilling zinc from the silver-gold-zinc crusts obtained in the Parkes process of lead desilverization. These pots were expensive and short-lived and it was hard to regulate the heat in the small furnace units. Metal losses were large and the quality of the produced zinc uncertain. The pots cost around $40 each, had a life of only 30 days, and required 33 hr. for distilling one charge of 750 lb. This process could not be adapted to mass production for obvious reasons.

Almost every smelter in the Kansas-Oklahoma district tried redistilling in one way or another; some used regular ore furnaces temporarily, by reversing the slope of the retorts and setting their back ends on to lower shelves. All of this company's branch smelters redesigned the tile lining and shelves and, in the construction of new furnaces or the repairing of old ones, new equipment was installed, making it possible to use a block of furnaces for either ore smelting or redistilling of metal as desired. Such expedients, however, were never as satisfactory as the main redis-

tilling plant, which was erected as a self-contained unit complete with all auxiliaries, including separate air fans, gas lines and pressure regulators. Mix-up in the destination of metals, contamination by sweepings, dust, ore-furnace tools, and fuels etc. were entirely avoided. Any one familiar with the usual zinc-smelting plants will readily appreciate this point in the light of the painstaking cleanliness and orderliness required for the successful and faultless production of highest grade zinc.

DISCUSSION

G. E. Dalbey, East Berlin, Conn.—If the ordinary galvanizing dross, that is dipped from the bottom of a galvanizing pot, running about 10 per cent. iron, were redistilled, how much zinc would you recover? How much zinc would the dross residue in the retort hold, and in what shape would it be?

Kurt Stock.—Do you mean metal of 90 per cent. zinc + lead and 10 per cent. iron? Metal with 10 per cent. iron is, of course, rather hard to melt by itself and is apt to be mushy after melting. It can be diluted in one of these large settling tanks to a point where it will readily melt and segregate. You will then obtain in the bottom most of the lead, which never holds more than 2 per cent. zinc. The iron-zinc is in a mushy condition above it, and can be handled readily, even if the iron content is above 10 per cent. This material can be distilled like any other metal in retorts.

G. E. Dalbey.—You would not find it practicable to redistill that 10 per cent. iron dross direct?

Kurt Stock.—You can do that, but the other method is preferable, as you save the lead and obtain a better spelter in the final distillation.

G. E. Dalbey.—How much zinc would remain and what would be the analysis of that residue?

Kurt Stock.—Practically no zinc whatever; nothing but iron, some lead, and other non-volatile impurities. No zinc whatever will remain after distillation at sufficiently high temperatures.

High Zinc in Lead Blast-furnace Slags

By Fred E. Beasley,* Kellogg, Ida.

(New York Meeting, February, 1925)

Metallurgists have, in the last ten years, overcome many difficulties of high zinc in lead blast-furnace slags. This problem was brought to the front at the close of the war, by the price obtained for lead and the high cost of labor, fuel, and flux.

The Port Pirie plant of the Broken Hill Associated Smelters, Australia, early in 1919 had increased the zinc oxide in its blast-furnace slags from 13.5 to 20 per cent., at the same time reducing the iron oxide in the slag from 33.5 to 25.6 per cent. These results were obtained by the addition of 10 to 12 per cent. granulated slag to the roaster charge, improved conditions of the crushing, mixing, and roasting of the constituents of the sinter. By experiments and improvements, the practice at this plant has developed a normal slag that carries 22 per cent. zinc oxide, and at times runs as high as 33 per cent. zinc oxide, with only slight furnace trouble. The granulated slag is used not only as a diluent to the sulfur in the roaster charge, but on account of its value as a slag-forming material and the physical properties it imparts to the finished sinter. The ore is mixed with flux and given a double roast. All the first roasting is by sintering with the Dwight & Lloyd machines. The final roasting is performed partly by Dwight & Lloyd machines and partly by H. & H. pots. The charge to the blast furnace consists chiefly of the final sinter, slag shells, siliceous and non-bearing sulfur lead ores. High blast and ore columns are the practice. The greatest care is taken to obtain in the final sinter as low a sulfur content as possible.

Attracted by the success of the Port Pirie plant, The Consolidated Mining & Smelting Co. of Canada, at Trail, B. C., in 1920 treated its crushed primary sinter with about 15 per cent. granulated slag. The Trail smelter at this time was short of ore and a large part of the charge to the roasters consisted of the zinc-plant residue having the following analysis: 12 to 16 per cent. lead, 12 to 16 per cent. zinc, and 25 to 30 per cent. iron. The lead in the final sinter was low and the physical condition was so bad that all the sinter had to be screened before it could be charged to the blast furnace. Also it disintegrated on being trammed and dumped

* Bunker Hill & Sullivan M. & C. Co.

into the furnace, which caused furnace trouble. After the addition of the granular slag to the crushed primary sinter, the final sinter while lower in lead content had a better physical condition and gave far less furnace trouble. A typical slag at that time consisted of about the following analysis: Pb, 1.2 per cent.; Zn, 14.0 per cent.; insol., 20.0 per cent.; Fe, 32.0 per cent.; CaO, 10.0 per cent. Today, the slags carry as high as 22 per cent. zinc and no troubles arise, provided the iron and sulfur are correct. At Trail, the double roast is done by means of Dwight & Lloyd machines. The granulated slag is still added to the second roast feed. As the lead in the charge is much higher now, the use of the granulated slag is prompted by the physical condition of the final sinter and the advantage gained in operating the furnaces.

The Burma Mines Co. smelter at Namtu, Burma, also sought to reduce the ironstone added to the furnace and to dilute the sulfur contents of the roaster feed by the addition of granulated slag to the feed of the primary roasters. No advantages were gained; but greater difficulty resulted in crushing the primary sinter and higher sulfur content in the final sinter. The dilution of the sulfur contents of the primary roast feed was solved by the addition of 10 to 20 per cent. of crushed secondary sinter or crushed furnace barrings. During August, 1921, 2871 long tons of furnace barrings crushed to 1/4 in. were used on the primary roaster feed as a sulfur diluent. An analysis of the crushed barrings was: Ag, 18 oz.; Pb, 28 per cent.; ZnO, 23.3 per cent.; FeO, 19.3 per cent.; S, 8.0 per cent.; insol, 11.2 per cent.

The four furnaces, with a loss of only three days out of 124, smelted 12,070 long tons of sinter produced with these barrings. An analysis of this sinter was: Ag, 31.9 oz.; Pb, 32.8 per cent.; Zn, 22.6 per cent.; FeO, 17.0 per cent.; SiO_2, 11.0 per cent.; S, 3 per cent. The furnaces produced 4276 long tons of bullion; the slag had about the following analysis: Ag, 0.6 oz.; Pb, 4.2 per cent.; ZnO, 27.2 per cent.; FeO, 30.2 per cent.; SiO_2, 23.2 per cent.; MgO, 4.4 per cent.; CaO, 5.0 per cent. It was interesting to note that even without a baghouse or a Cottrell plant, the silver recovery was about 90 per cent. and the lead about 84 per cent.; also the barrings used had been exposed to the tropical climate and weather for years and were in a very poor physical and chemical condition. The furnaces ran well until more lime was added, in an attempt to clean some of the lead from the slag; this was successful in lowering the lead but the furnaces slowed up until the extra lime was taken off the charge.

The practice at Namtu is to obtain the primary roast by Dwight & Lloyd machines, crush and reroast part in H. & H. pots and part by secondary Dwight & Lloyd machines. The sinter contains all the charge to the blast furnace, except the lime, which is added to the furnace with the coke. The return dross also is charged but no shell slag.

The ore, blast, ore column, size and type of furnace used by these plants vary in such a manner as to have no general bearing on each other in regard to high zinc in slags. They are all successful in operating with slags that run as high as 22 per cent. zinc, and at times much higher. The writer, through associations with metallurgists of these plants and from observation and experience at the Trail Smelter and the Burma Smelter, wishes to present the following conclusions, which are based on the procedures found necessary in these plants in producing high zinc in lead blast-furnace slag:

Thorough crushing and mixing of all the constituents of the primary feed.

A dilution of the sulfur contents of the primary roast feed to 10 to 14 per cent. sulfur by the addition of some such material as granulated slag or crushed sinter.

Special attention given to the moisture of the roaster feed.

The sulfur contents of the final sinter should be under 2 per cent.

The sinter charged to the furnace should have very few fines.

The iron in the slag should be slightly higher than the zinc.

DISCUSSION

R. C. Canby, Wallingford, Conn.—About 1896, there was a good deal of discussion about high zinc in lead-furnace slags and the *Engineering & Mining Journal* had an article pretty well covering the ground and showing slags varying from 15 to 20 per cent. and over zinc oxide. The interesting thing in this paper is that there is no reference to any particular difficulty; those of us who smelted in the West in those days when zinc in the charge was high and the lead was low had a great many difficulties. The particular thing is that every charge in the furnaces mentioned in this paper is a sintered charge.

About 1912, I had rather an interesting experience with some work that Dwight & Lloyd were doing with roasted pyrite ore from acid plants. There was no possibility of smelting it in the blast furnaces. Experiments treating that material after sintering showed remarkable fusibility. The material had defied the reverberatory furnace because there was no reducing action and the blast furnace because of its fineness. In describing this sinter, at the time, I referred to the sinter as "predigested furnace feed."

In the slags referred to, in 1896, it was a question about high lime in zinc-bearing slags. In the work to which I referred particularly, at that time we had to have a high lime and those slags containing 20 per cent. zinc oxide carried sometimes as high as 23 or 24 per cent. of CaO. Herman A. Keller[1] had previously referred to a high lime, with high zinc.

[1] The Desilverization of Lead Slags. *Trans.* (1892) **21**, 71.

We had to carry high lime in the smelting to which I referred since we had no iron and it was also necessary to have a low specific gravity. The high lime gave a much better separation on account of the low specific gravity; we used a little more fuel—about 18 per cent. Of course, with this predigested charge, while the fuel in the smelting charge is not given, I suppose it is much lower than that.

FRED E. BEASLEY.—High lime, high zinc, and sulfur will freeze a furnace, for this reason low CaO, from 15 to 5 per cent., is the practice in producing a high-zinc slag. Coke at these plants averaged 9 to 12 per cent. of the charge.

R. L. LLOYD, New York, N. Y.—Difficult slags will also be encountered in copper practice. Equivalent slags I have made were much over 20 per cent. zinc, using sintered material almost to 100 per cent. In making a difficult zinc, or any other difficult slag, the rate at which the furnace runs will affect to a large extent the ability to handle that particular slag. A very fast driving furnace will handle a difficult slag that a slow driving furnace will not and much of the ability to handle difficult slags comes from the fact that with a sintered charge, invariably, the furnace is driven so much more rapidly than with a fine charge.

CARLE R. HAYWARD, Cambridge, Mass.—One important thing is the temperature in the furnace or the rapidity of driving. When visiting Trail two years ago I was astonished at the high-zinc slags they were making, also at the temperatures observed in the lead furnace. They were running with a top much hotter than the customary practice, but the slags were running well, and they have made slags even higher in zinc than those noted here.

At the laboratories of the Massachusetts Institute of Technology last year, a study was made, by H. T. Mann, of the equilibrium of ZnO, CaO, FeO, and SiO_2 and various replacements of the bases one by the other. These results will doubtless be published in the near future. They brought out the fact that there were several groups of slags that, as far as the melting points and fluidity were concerned, could be used in lead smelting and run high in zinc, but the range of those slags was astonishingly narrow. We found that, having established a slag that would fuse within the range of ordinary lead-furnace practice, by varying some one of the constituents 1 or 2 per cent, one way or the other, the fluidity would either change or the melting point would rise to a temperature that would be undesirable in the lead blast furnace.

I believe that the figures obtained would be confirmed in a lead furnace and that some of the troubles found in lead smelting with high zinc in the slags have been due to the fact that the very narrow range of composition possible in the slags used has not been fully recognized.

I say narrow range; at least two and possibly three groups of slags can be used, but in either of them slight changes in composition are disastrous.

R. C. Canby.—This paper says the iron must be slightly in excess of the zinc; was that one of the things you noticed?

Carle R. Hayward.—That was true in some cases. There is another group of slags where that was not true.

Fred E. Beasley.—With varying constituents, slightly higher iron than zinc in slag acts as a factor of safety on a commercial scale and gives continued operation.

G. E. Dalbey, East Berlin, Conn.—Once I smelted some foundry ashes and refuse in a circular 36-in. blast furnace to black copper. The slags from this operation ran about 20 to 25 per cent. zinc oxide. We had pretty good luck as long as we kept things moving and the furnace hot. If for any reason the furnace was slowed down, it was practically impossible to get the furnace back to good running order again; but if kept hot we had practically no difficulties. The iron oxide in the slag went about 37 per cent.

Arthur S. Dwight, New York, N. Y.—The function of the granulated slag added to the raw charge to be sintered is twofold. First, it acts as a diluent in separating, one from another, the little individual particles of sulfide and preventing their fusing together in the first heat of roasting and by holding them apart permitting each particle to be instantly burned up, you might say, as the zone of ignition reaches it; second, it gives a certain amount of slag-making material, which can unite with the oxide produced in the preliminary, or roasting, phase to form a coherent sinter in the final or sintering phase. Those two factors are necessary to produce good results and a coarse sinter for the blast furnaces. The author speaks of the successful use of granulated slag at Port Pirie, Australia, while in the smelter at Namtu, Burma, the crushed slag was not so helpful. He fails, however, to give the corresponding analyses. I venture to say that in the one case there was a deficiency of silica or fusible material in the charge while in the other case there was an ample amount, and the slag was unnecessary and consequently took up space and was therefore undesirable.

The final results obtained in those plants, each by its own procedure, was a satisfactory furnace product. It was that product that did the work, because it brought about a certain set of conditions in the blast furnace that made it possible to carry high zinc in slags.

The author says that, in one place, they had to screen out all the fine material so as to have a coarse charge. He also speaks of the high blast that was helpful in fast driving, which several have mentioned as necessary to carry through a slag high in zinc, and that it permitted the

furnace to run on a lower fuel charge. All of these factors made to the same end. When carrying a high fuel charge in a blast furnace smelting high-zinc ores, the tendency is to reduce the zinc to metal in the lower part of the furnace and give it a chance to combine with whatever sulfur there may be present to form regenerated zinc blende, which will make trouble. But by having an open charge, driving fast, and carrying a lower fuel percentage excessive reduction is avoided and yet the necessary heat for smelting is obtained. Thus by keeping the zinc in the form of oxide it is possible to carry off a maximum amount of that zinc in the slags without the formation of products which are detrimental to the successful running of a lead furnace. The chemical condition of that slag is likewise extremely important. There are very narrow limits in the range of analysis that will successfully carry a high percentage of zinc.

My own experience has been based on empirical considerations but I think that there is a scientific solution, upon which, no doubt, the results of the investigation that has been made at the Massachusetts Institute of Technology will throw a great deal of light. We will welcome the publication of these results.

I will mention a personal experience of this problem. About the time of the Spanish War, the company by which I was then employed had a lead mine in Northern Mexico, just south of the big bend of the Rio Grande River, and was shipping the ore to a smelter in this country. It carried about 35 per cent. lead, a small amount of silica, a small amount of zinc, and a little iron. The company decided that the ore could be smelted more advantageously on the spot, so I was instructed to build a smelting plant and turn the ore into bullion on the spot. We were about 100 miles from the nearest railroad—the Southern Pacific in Texas. It was, therefore, necessary to build a wagon road from the railroad to the plant and a wire-rope tramway across the Rio Grande, which was very wide at that point, and then build a smelter on the Mexican side in as simple and expeditious a way as possible.

When we came to consider the smelting of that ore alone, because there were no other ores available, we found that taking out the lead left a residue in which the amount of zinc more than equalled the amount of silica, and there was no other silica handy. It was in the midst of a limestone desert.

We solved the problem after a good deal of experimentation. We found, in the first place, that the furnace charge must be kept very open and the fuel at an absolute minimum. To do that we used the best coke we could get that would stand the long haul by teams from the railroad with its least breakage and supplemented the coke on the charge with big pieces of cord wood, which we put down in the center of the furnace vertically, so as to keep a very open charge. I decided that

everything possible should be done to avoid reducing the zinc. We had a little sulfur in the ore so it was necessary to reduce iron to take care of that and clean the slag. So, figuring out, in a general way, that it took about a ton of coke to make a ton of iron, I decided to bring in scrap iron instead of part of the required coke. Scrap iron was just about the same price as coke and, assuming that it was equivalent ton for ton, we could bring in the iron already reduced rather than reduce it ourselves in the blast furnace. So by means of this "predigested iron," to use the author's expression, and using local cord wood to replace part of the coke and also to help keep the furnace charge open, we were able to smelt slags running up to 25 per cent. zinc oxide, which is about the highest I had ever been able to handle.

That slag ran about 25 per cent. silica and 25 per cent. zinc oxide, and enough iron to make up the proper composition. That experience taught me a lesson in the matter of handling high-zinc oxide in the lead furnace slags and, I believe that if this principle is kept in mind, it may prove a guide to the solution of some of the tough problems that occasionally confront us in smelting ores high in zinc.

As to the chemical composition and the types of slags that will best carry oxide of zinc, I believe that the zinc is present in slag in the form of a dissolved zinc spinel; I have several times worked out interesting conclusions from high-zinc slags that were given me and which I knew to be well running slags. In such reasoning, we must start with a slag that we know is good, and work back. Figure first the sulfur with the necessary iron to cover it as matte; then figure the alumina to zinc oxide to form alumina spinel, $ZnOAl_2O_3$, then figure the balance of the zinc. to $ZnOFe_2O_3$, then figure the balance of the iron as FeO to combine with SiO_2 and CaO in the usual slag formula. You will have SiO_2, FeO, and CaO. In most of the cases where I have applied this test, I have found a resultant slag formula which corresponded very closely to the slags that the lead smelters generally recognize as good types with a dissolved zinc spinel. In other words, they have almost invariably come right down to first principles and well accepted formulas. Whether this principle will prove to be a step in the establishment of proper working theory of slags for handling zinc I cannot say, but it has helped me very much.

C. S. Witherell, New York.—What do you consider fast running of the furnace?

R. L. Lloyd.—Anything under 7 tons to the square foot I would not call fast. I was speaking of copper, particularly, for I am handling such slags.

E. P. Mathewson, New York, N. Y.—With the sintered material that the author mentions, about 275 onts to the ordinary furnace or

say 7 tons per square foot of hearth area. When the charge smelts rapidly, there is little trouble due to high zinc.

FRED E. BEASLEY.—The Burma Mines Co., Namtu, Burma, smelts 3 to 4 tons. The Consolidated Mining & Smelting Co. of Canada, Trail, B. C., smelts 5.5 to 6 tons. The Bunker Hill smelter at Kellogg, Ida., when producing a slag containing 10 per cent. zinc oxide, smelts 4.5 to 6 tons, but when producing a lower grade zinc-oxide slag smelts as high as 10 tons.

ARTHUR L. WALKER, New York, N. Y.—The analysis of Burma slag shown on page 920 indicates a lead content of 4.2 per cent. We would hardly consider that a satisfactory slag from a metallurgical standpoint though undoubtedly it is from a commercial standpoint. It is probably more economical to produce a slag high in zinc even if the lead is also high.

It is recognized that the form in which the zinc is present in the slag has a distinct bearing on its character. If a high percentage of zinc is present as a sulfide, there is apt to be trouble; if present as oxide, a much more fluid slag will result. That can be illustrated by the results obtained at a copper smeltery, located near Newark, N. J. At that plant, they are treating a material that contains almost all the common metals and some of the rare ones, but it does not contain an appreciable amount of sulfur. It is an oxide-smelting operation pure and simple. Now, we all know that in smelting oxidized copper ores it is impossible to make a slag that is low in copper. Doctor Douglas, in the good old days down in Arizona, used to say, "We never made a slag that contained less than 2 per cent. of copper, but when we quarried that slag dump for resmelting years afterwards, we always obtained 3 per cent. from it." When smelting an oxide copper ore or material, we necessarily make a slag high in copper.

At this plant to which I referred, the slag will contain from 13 to over 20 per cent. zinc oxide. But the zinc content of that slag does not seem to have any bearing on its copper content. When the zinc is high the copper may be lower. For example, the average composition for the slag for one month was 16.5 per cent. zinc oxide and 1.3 per cent. copper—a very favorable result for an oxide-smelting proposition. The next month the zinc oxide content was 13.7 per cent. and copper content 1.5 per cent. In the next two months, it increased to 18.5 per cent. and the copper content went down, which clearly indicates that the effect of zinc as an oxide in slag, within certain limits, is not detrimental. When the zinc content of the same slag is much above 20 per cent., however, the copper will go up. The average composition of the slag in question varies from 27 to 30 per cent. SiO_2, from 30 to 27 per cent. FeO, and from 13 to 16 per cent. CaO.

Fred E. Beasley.—The extra high lead content was due to special run of barrings; the normal slag contained 1.5 to 3 per cent. lead. Native labor in making sinter and feeding and topping furnaces accounts for higher lead loss in slag than in a white man's country.

B. M. O'Harra, Rolla, Mo.—I believe it has been found, in roasting zinc ores, that a Dwight & Lloyd roaster is especially efficient in breaking up zinc sulfate; at least it gives a product that is very low in zinc sulfate. Would that have any bearing on the formation of zinc sulfide in the blast furnace?

R. L. Lloyd.—It undoubtedly has, because zinc sulfate would reduce to the sulfide readily. Large quantities of sulfate result in large quantities of sulfide being reduced. In the practice of a smelter with which I am connected, where sulfates are present sulfides invariably result.

C. P. Linville, Elizabeth, N. J.—It might be well to bring out a little more clearly just what this predigestion does. Zinc oxide in the presence of carbon monoxide at furnace temperatures is easily reduced to zinc that combines with any sulfur present to give zinc sulfide. This zinc sulfide goes into the well-known mushy material that gives trouble. If, by predigestion, we convert the zinc into zinc silicate or zinc ferrate, we obtain a combination not easily reduced by carbon monoxide, and consequently the formation of zinc sulfide is prevented. When such material containing lead, also as silicate, is melted to a slag in the presence of solid carbon, the lead is so much more easily reduced than the zinc that it is possible to get complete lead reduction without any zinc being reduced. On account, however, of the preformed silicates making a more rapidly fusing slag, there may be greater danger that, with rapid driving, the lead reduction will not be completed, and high-lead slags will be obtained. Perhaps this may account for the high leads reported in the zinky slags mentioned.

The point I wish to make is that predigestion has done a considerable part of the work that otherwise would have to be done in the furnace itself, by combining the zinc with silica, iron, and other things into compounds not easily reduced by carbon monoxide or solid carbon. As zinc sulfide can only be produced by the action of sulfur or sulfur compounds on metallic zinc, such predigestion will, therefore, effectually prevent most of the troubles caused by zinc.

Arthur S. Dwight.—In most of the large lead-smelting plants in this country, the entire charge for the lead blast furnaces, including fluxes and everything that goes into the charge, is automatically proportioned, thoroughly mixed, and heated on the sintering machines; consequently there is likely to be a considerable formation of silicate of lead. However, on account of the very open cellular structure of the

D. and L. sinter the reduction of lead is very complete, because we know that the average run of lead slags in this country are very low in lead; they have to be so or the company would soon go out of business. That is sufficient answer to the question as to behavior of the lead in the presence of silica.

In connection with this question of sintered lead ore, I might add that in almost all cases less coke is carried on the furnaces than was required when the ore was in the earthy condition and unsintered. So in spite of the fact that the lead may be very largely in the form of silicate of lead, if sufficient silica is present to do that, the lead will be thoroughly reduced even with less fuel than before.

R. C. CANBY.—When I first knew Colonel Dwight, one of the things that he particularly dwelt on was the influence of the gases in lead smelting. From the literature that we have in America on lead smelting, we often are too apt to form an idea simply of the carbon. I have a little Spanish book on metallurgy; the practice it describes is very crude, but its appreciation of the descending charge and the ascending gases is more complete and more illuminating than anything in American literature and that is very important when you consider what has been called the proper porosity of the predigested charge.

A New Roasting Furnace for Zinc Flotation Concentrate

By Charles H. Fulton,* Rolla, Mo. and J. Burns Read,† Denver, Colo.

(New York Meeting, February, 1925)

A previous article[1] by the authors contained a general description of the new roasting furnace herein described but it did not go into detail as to the metallurgical behavior or the results obtained. Believing that such information would be of great value, they have elaborated on the subject and have given many unpublished details.

The furnace described applies the principle of roasting finely divided zinc-sulfide ores, now produced in large quantity by the flotation process, in gaseous suspension; that is, the ore particles are carried, in suspension, in a current of air and gaseous products of the roast. The relatively great fineness of flotation concentrate presents difficulties and problems of roasting in furnaces of the ordinary type; the fine ore is forwarded through the furnace in the form of a shallow bed and its very fineness leads to dense impervious bedding which prevents oxygen from reaching the interior of the bed, thus unduly lengthening the time of roasting and preventing the elimination of the last of the sulfur. The fineness of the concentrate, normally, should lead to a rapid and complete roast, for the speed of roasting is a function of the surface exposed to oxygen, which surface is greatest, per unit of weight, in very fine material. The difficulty in bed roasting is to get the oxygen to the particle. If the fine ore, during the roasting, could be freely suspended in oxidizing gases, full advantage could be taken of the great surface conferred by its fineness. This fundamental idea, of course, is not new, for the Stedtefelt furnace, familiar to the older metallurgists, is an example of it; but the manner in which this is accomplished may be new.

The numerous efforts to roast in gaseous suspension show that the idea is attractive; in fact, an analysis would indicate that it is the most reason-

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† Metals Exploration Co.

[1] Roasting Zinc Concentrates in Suspension. *Eng. & Min. Jnl.* (1920) **110**. **405**.

able way to effect the oxidation of ore, provided certain difficulties can be overcome. Two objections against such a method that formerly had much weight were the cost of fine grinding the ore, also the fact that the finely ground product, even after roasting, was not the best condition of material for further metallurgical operations. The objection of costly grinding, however, has been removed by the production of great quantities of flotation concentrate, which in point of fineness present a material that is ideal for roasting in gaseous suspension.

The inception of the experiments described here is due to David B. Jones and March F. Chase.[2] The idea of the general type of furnace and process was suggested to the authors and the experimental work was carried out in the metallurgical laboratories of the Case School of Applied Science at Cleveland in 1915–6. The original plan was to make a furnace for roasting zinc-blende flotation concentrate that would use the heat value of the sulfide to accomplish the roasting and to produce a gas suitable for making sulfuric acid; *i. e.*, of sufficient concentration in SO_2 and practically free from the products of carbonaceous combustion. Autoroasting of sphalerite is theoretically possible,[3] and also practically, as was demonstrated in the experiments set forth.

A diagrammatic drawing of the roasting furnace and accessory apparatus as erected is shown in Fig. 1. Here *A* is the furnace proper; *B* the two stoves, heated by natural gas, that preheat the air; and *C*, the Cottrell electric precipitator for the precipitation of flue dust and fumes carried from the furnace by the gases, which in a commercial plant would pass to a sulfuric-acid plant. At *H* is the gas supply for the stoves; *X* is the dust chamber, and *G* is the cycloidal blower that furnishes air to carry the ore in suspension in the furnace. The dried, preheated ore (60° to 100° C.) is charged into the hopper 1 whence the endless screw 2, operated by a variable-speed electric motor 3, discharges it into a pipe 4, directly above the nozzle 5. A stream of high-pressure (20 to 60 lb.) moderately preheated air is discharged through this nozzle in such quantity as to carry readily the fine ore in suspension into pipe 7, on the injector principle. Pipe 7 is of larger diameter than pipe 4 and is lined with refractory material; it serves as the main injector pipe into the furnace. Air, heated to approximately 800° C., passes from one of the stoves *B* to the injector pipe 7, through the supply pipe 9; this is the main air supply for roasting the ore.

[2] The work was carried out for Mr. Jones and the authors wish to make grateful acknowledgment to Mr. Jones and Mr. Chase for much aid and many valuable suggestions.

[3] J. W. Richards: "Metallurgical Calculations," 1 vol. ed., 620. McGraw-Hill Book Co., New York.

W. R. Ingalls: Autogenous Blende Roasting. *Min. & Met.* (1922), 3, 11.

The amount of air supplied is governed by two principles: (1) The quantity must be correct to roast the ore and to furnish a gas of the correct composition for the manufacture of sulfuric acid. Every pound of

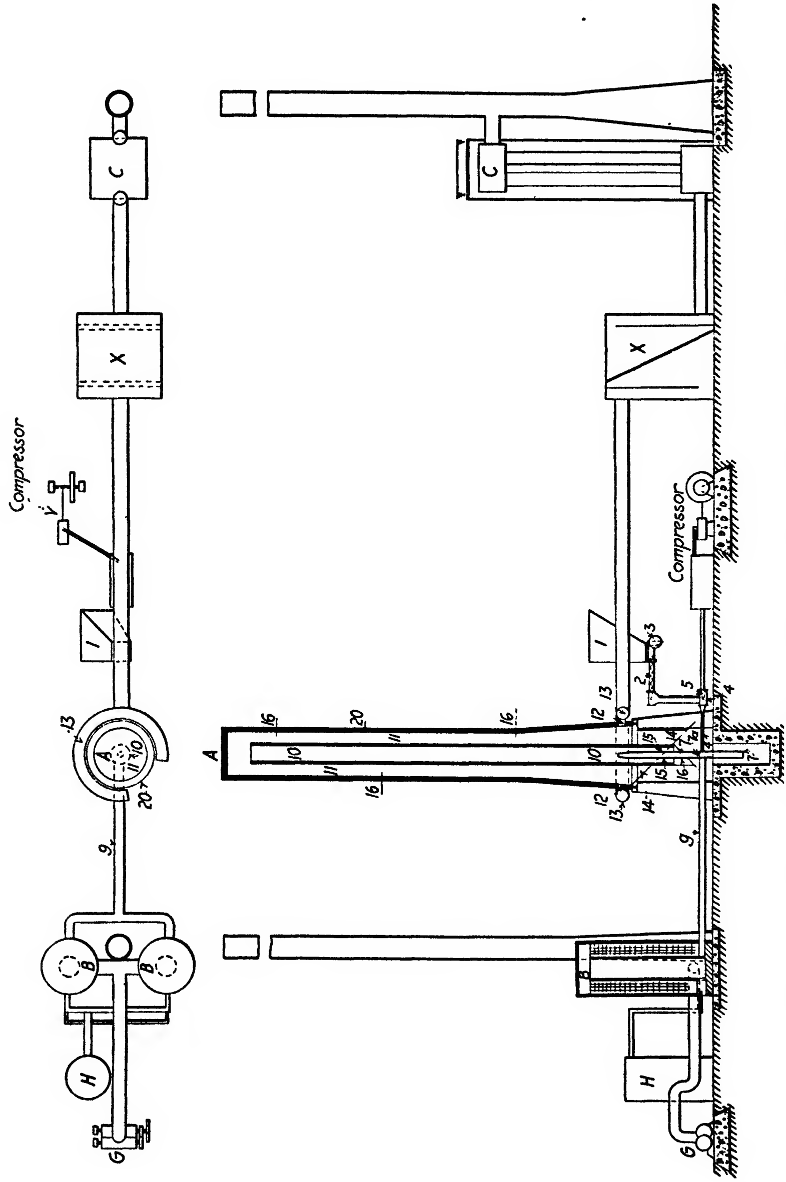

FIG. AG 'ATIC VIEW O ROA NG FURNACE AND ACCE RY APPA

sphalerite requires 35.7 cu. ft. of air (standard conditions) to convert the zinc to oxide, the sulfur to dioxide, with enough more oxygen to convert this into the trioxide. Some excess must be carried; in the experi-

ments from 41 to 55 cu. ft. and sometimes 75 to 100 cu. ft. was used, as measured by a meter. (2) There must be such a relation between the quantity of air per minute and the area of the riser tube 10, that the velocity of the ascending air current will be enough to carry the largest ore particle to the top of this tube and over the edge. Fig. 2 gives definite data on this point for sphalerite. Fortunately the requirements for both conditions can readily be fulfilled.

The mixture of ore and high-pressure air from pipe 4 enters the main injector pipe 7 with a rotary motion and is caught by the ascending hot

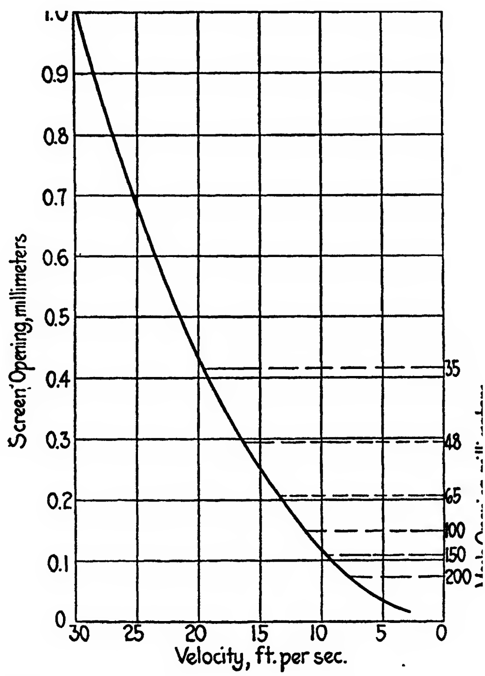

FIG. 2.—SPHALERITE SUSPENSION CURVES FOR SPHERICAL SHAPES; SPECIFIC GRAVITY 4.1. PLOTTED FROM RITTINGER'S FORMULA.

air from the pipe 9 and injected into the riser tube 10. The fundamental idea is to have the temperature of the ore-air mixture at the ignition point of zinc sulfide, which varies between 650° and 810° C., depending on the size of the particle[4] as it leaves the injector tube to enter the riser tube, so that the full time of the ore particle in the furnace will be available for oxidation. After leaving the riser tube 10, the ore particle falls into the annular space 11, the area of which is large so that the natural velocity

[4] B. M. O'Harra, William Kahlbaum, E. S. Wheeler, and W. J. Darby: Effect of Oxygen-enriched Air in Roasting Zinc Ores. Issued as Paper No. 1302-M, with MINING AND METALLURGY (March, 1924).

of fall shall not be augmented by the velocity of the descending gases. It is the belief of the authors that the gas envelope surrounding the ore particle is constantly changing; thereby causing fresh oxygen to be supplied to the particle.

The time necessary for the roasting is furnished by the passage of the ore up the combustion tube 10 and its fall into the annular space 11. This time depends on the height of the furnace, the length of the path of travel being practically twice the height of the furnace, also on the velocity of the ascending air current in the combustion tube. Assuming a definite ratio of cubic feet of air per pound of ore, the velocity will be determined by the area of the combustion tube. Definite figures on this point are given later. In any given furnace, *i. e.* a fixed area of combustion tube, there is a certain variation allowable in the velocity of the ascending gas current, obtained by varying the amount of air, which will then vary the time of the ore in the combustion tube. Too high a velocity, obtained either by too much air only or too great an ore feed with its corresponding increased amount of air, will shorten the time element so much that the sulfur is not sufficiently eliminated. The greater part of the ore collects in the hopper 14; the gases and fine dust pass, through openings 12, into the flue 13, thence to the settling chamber *X*, where the coarser dust is settled out, thence to the Cottrell precipitator *C* for the precipitation of the finest dust and fume.

Thirty-foot Experimental Furnace[5]

The design of the 30-ft. experimental furnace was, as far as possible, based on the results obtained in the previous work but was limited by lack of space and the capacity of the stoves, blowers, gas supply, etc. The stoves had been erected for the small furnace already described and were known to be inadequate for the larger furnace, but no space was available for enlarging them. It was also desirable to keep the expense as low as possible, so that some things that would have aided in the work were omitted.

The furnace consisted essentially of a brick stack (Fig. 3) approximately 30 ft. in height from the base plate to the top of the cover arch. The base plate and support rested on 4-ft. reinforced concrete posts, thus making the total height about 35 ft. The space between the posts provided room for the calcine hoppers and air and feed inlets and a pit provided the additional space necessary for the cleaning of tools and for making repairs.

The stack was built of two concentric firebrick circles 24 and 36 in. internal diameter; the space between these circles was filled with mineral wool. Somewhat larger circle brick were used near the bottom of the

[5] U. S. Pat. 1273844.

stack to increase the stability. No steel shell was placed outside of the brick, though such a shell would have aided greatly in the construction

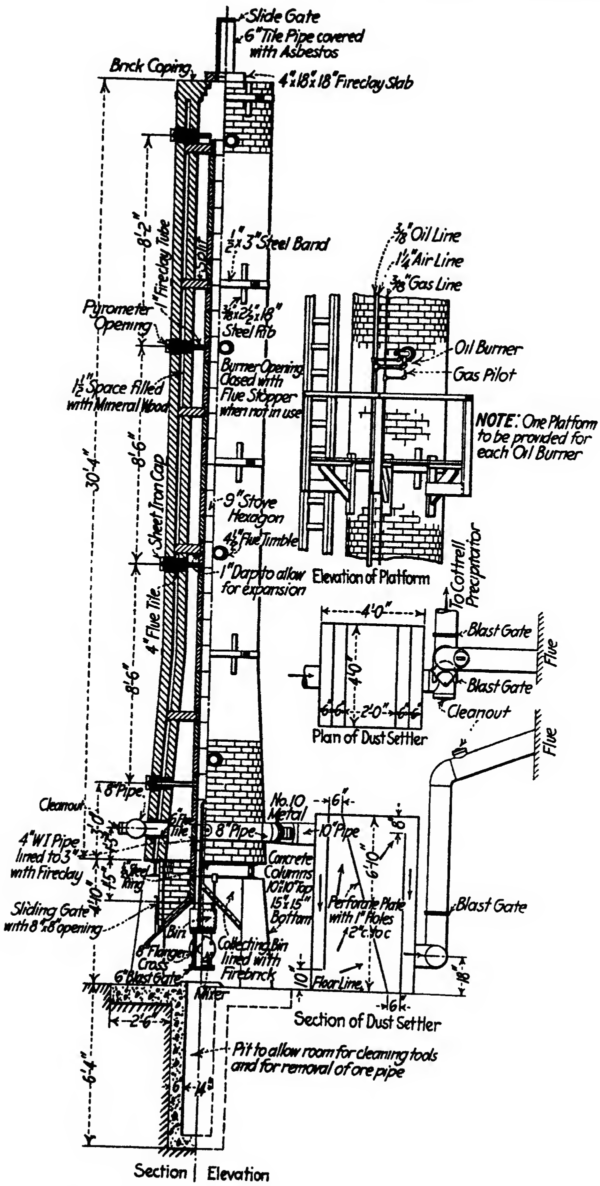

Fig. 3.—Experimental roasting furnace.

of the furnace and in carrying on the tests. The top of the stack was closed by fireclay slabs, a small circular hollow tile being set at the center;

a gate at its top permitted the interior of the furnace to be watched while operating. Two hoppers at the bottom of the stack collected the greater part of the roasted ore. Above these hoppers, and spaced at equal intervals around the stack, were four openings to the flue that led to the settler and to a small Cottrell precipitator.

Concentrically with the walls of the stack was placed the riser, or combustion tube, which extended from below the hoppers to within about 5 ft. of the furnace top. This tube, in the earlier trials, was made of

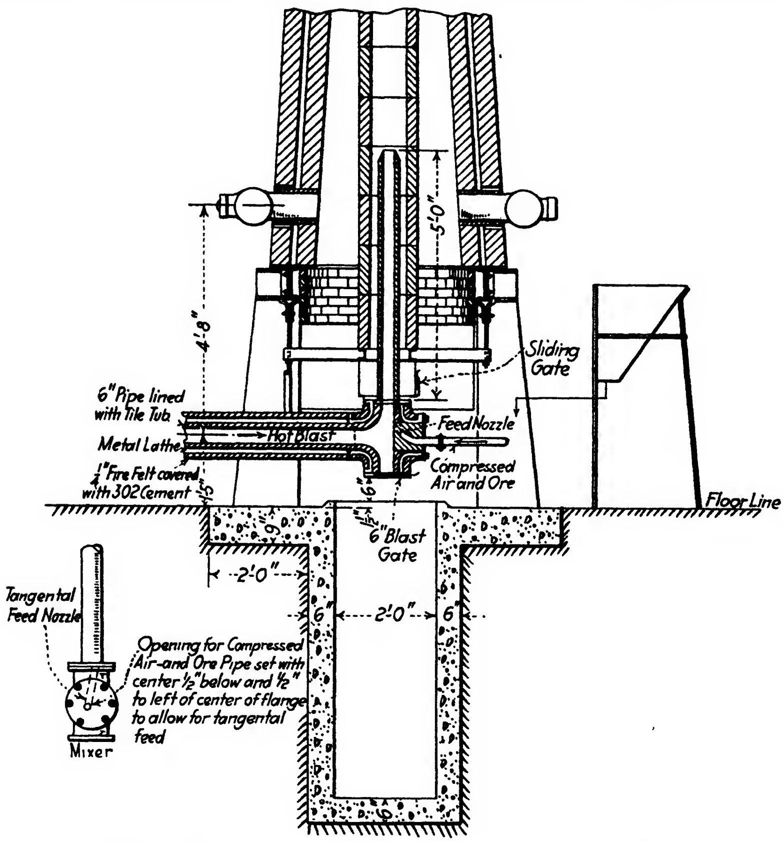

Fig. 4.—Section through mixer of experimental furnace.

9-in. hexagon stove tile but later 12-in. cylindrical tile was used. The annular space between the combustion tube and the stack walls served as a downtake for the products of the roast.

The injector nozzle entered the bottom of the combustion tube for about 5 ft., thus placing its delivery point about 2½ ft. above the base plate of the furnace. The nozzle was a 2-in. fireclay tube and connected at its lower end with a pipe or mixer, into which the air and ore were injected from the stoves and feeder respectively.

Stoves

The two stoves were of the central combustion type, the combustion tube being made of 9-in. hexagonal stove tile. The checkers were made of 2 by 2 by 9-in. brick laid to provide the maximum heating surface. A 1/8-in. steel shell with top and base plates insured airtight conditions. The stoves were 4 ft. in diameter, and 10 ft. in height. The usual burner, cold-blast, hot-blast, and flue openings were provided; the stoves were heated with natural gas.

Hot-blast mains connecting the stoves to the mixer of the furnace were 6-in. iron pipe lined with 4-in. fireclay flue liners, and covered with heavy asbestos insulation. Connections were provided between this pipe and the cold-air supply so that the temperature of the air entering the furnace was always under control. A bypass was provided at one point so that the air could be sent through a rotary gas meter at intervals; the metering was done cold and corrections made to temperature and pressure.

Feeder

The feeder used was a modified Dunn pulverized coal feeder. Certain parts, originally made of brass, were later replaced by high-speed, hardened, tool-steel parts to avoid excessive wear from abrasion by the ore. A screw conveyor carried the pulverized ore from the bottom of a hopper to a pipe in which a suction was produced by a compressed-air jet issuing from a 1/8-in. or 3/16-in. nozzle past its lower end. The ore was carried, by an expanding compressed-air current, toward the mixer and injector pipe. The connection into the mixer pipe was made tangentially and also inclined upwards so that the ore and air mixture met the hot air from the stoves in a rising spiral and thus thoroughly mixed the hot air and ore before they entered the combustion tube.

Approximately 10 cu. ft. of free air compressed to 60 lb. per sq. in. was necessary per pound of ore to carry the ore from in front of the 1/8-in. or 3/16-in. nozzle into the mixer. At times, even this amount was insufficient to prevent stoppage of the pipe, so the amount of air was increased at intervals to remove any accumulations by the arrangement shown in Fig. 5.

Seven thermocouples were placed in the furnace: four being placed in the combustion tube as shown, one in the mixer just below the base of the injecting nozzle, one in the downtake at the exit to the flue, and one in the downtake 20 ft. from the base plate. Lead wires were run to a central galvanometer station where readings were taken throughout each test.

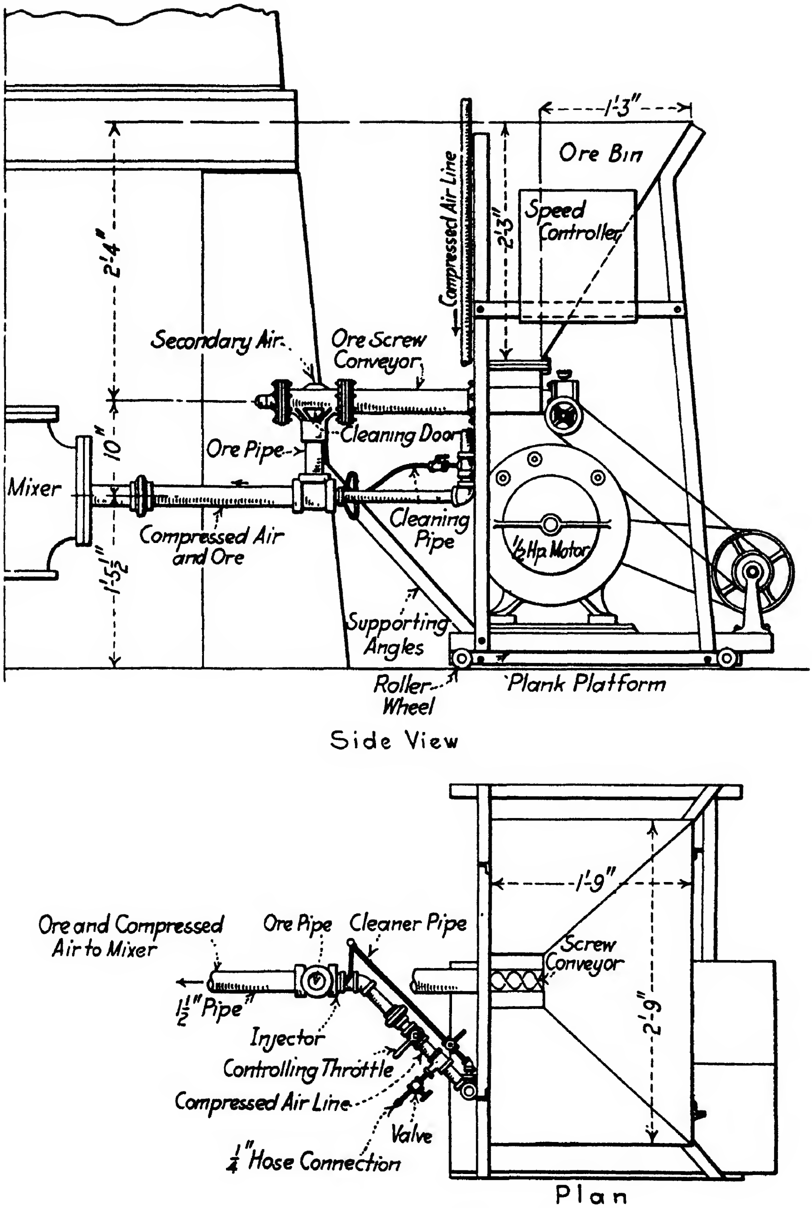

FIG. 5.—FEEDING DEVICE OF EXPERIMENTAL FURNACE.

TABLE 1.—*Furnace Record*
(12-in. Combustion Tube)

Time	Temperature. Degrees C.					Per Cent. Sulfur in Roasted Ore		Per Cent. SO_2 in Gas	Cu. Ft. Air per Pound Ore	Pounds Ore Fed
	Mixer	Combustion Tube Distance from Furnace Base								
		4 Ft.	12 Ft.	22 Ft.	28 Ft.	Hopper	Flue			
A.M.										
9.55	275	850	940	890	965	7.0	5.4	5.2	57.3	160
10.10	295	840	930	890	975			5.2		
10.25	375	830	930	890	975	7.1	3.5	5.3		
10.40	350	830	930	880	975			5.3		160
10.55	365	825	940	890	985	7.4	4.9	5.1		
11.10	365	825	940	890	995			6.9	51.2	
11.25	350	805	940	890	975	7.8	5.5	5.3		160
11.40	405	815	930	890	985			3.03	55.4	
11.55	395	825	940	900	1005	8.0	5.4	5.3		
P.M.										
12.10	315	830	940	900	1030					160
12.25	340	830	950	915	1030				55.4	
12.40	315	840	950	915	1040	5.1	5.0			160
12.55	350	830	950	925	1040			7.5		
1.10	350	830	955	930	1055	7.0	5.0	6.8	40.7	160
1.25	375	830	965	950	1085			6.8		
1.40	365	840	965	950	1110	6.6	4.8	5.6		160
1.55	375	850	975	950	1110	5.9	4.4	5.5		
2.10	375	850	985	955	1100	5.4	3.8	5.2	44.7	160
2.25	375	840	975	950	1100	2.5	2.2	3.8		
2.40	375	850	985	955	1125	2.5	2.3	3.9		160
2.55	365	850	985		1155	2.3	3.1	4.1	44.7	
3.10	375	850	995		1190	3.3	3.5			160
3.25	385	850	995		1195	4.3	3.8	3.2	32.6	
3.40	425	855	1010							160
4.10	250	855	1020		1125			4.5		160
4.15	215	855	1020		1135					
4.25	165*	865	1030		1120	4.3	3.7	4.5		
4.30	150	865	1030		1170					

* Lowering of mixture temperature due to shutting off the stoves. Cottrell apparatus in service during the run, results good.

General samples from the products accumulated during the run showed these sulfur contents:

	ENTIRE RUN	MORNING RUN	AFTERNOON RUN
Hopper	5.8	8.2	3.7
Flue	5.9		3.5
Settler	5.5		
Cottrell	6.0		

This run began 1 hr. before the time indicated (9:55) but conditions did not permit sampling, and adjustments caused unreliable results previous to those shown.

Total ore fed during the entire run, 2080 lb.; of this 160 lb. were fed before beginning the record.

Burners

Openings for oil burners were provided at intervals of 8 ft. throughout the height of the furnace. These openings were placed tangent to the inside circumference of the downtake. The burners were for the purpose of bringing the furnace to the operating temperature and were not used after such a temperature was reached and feeding of ore had begun.

The products of combustion of the oil heating were taken off at the top until the burners were going well, when the top was closed and the draft directed through the flues near the bottom of the stack. After a temperature of 800° to 1000° C. in the furnace had been reached, the burners were shut off, the burner openings closed, and the ore and air feed started. Adjustments of ore and air feed were then made as indicated necessary by the SO_2 content of the gas, temperature conditions, and quality of roasted product. The furnace responded readily to such adjustments, but the time permitted for the test was not sufficient to permit adjustments to the best results possible.[6]

Results

In order to increase the capacity, the 9-in. tube was replaced by a 12-in. This tube was of specially made tile with 1½-in. walls, which restricted the area of the downtake more than was desirable and probably resulted in slightly poorer results than could have been obtained if the diameter of the furnace had been increased in proportion to the increase in the diameter of the combustion tube. Such a change, of course, was impossible without completely rebuilding the furnace.

Table 1 gives the results of a test made with the 12-in. tube. The temperature at the top of the furnace increased beyond that which was desirable, so in the last run cold air was admitted at 20 ft. from the base plate, thus providing for a complete control of the temperature and preventing the hot top. When cold air was thus admitted, it was necessary to reduce the amount of air fed with the ore, which meant a lowering of the velocity in the combustion tube and resulted in an increase in the bottom temperature. This increased bottom temperature, in turn, permitted the reduction in the temperature of the air coming from the stoves.

It was thought that accretions would form in the combustion tube during the roasting but, with one exception, no trouble was encountered from this source, even though the temperatures at times were allowed to go beyond those that would be permitted in practice. Some little diffi-

[6] The furnace could not be operated for more than 12 hr. as power was available only during the day. The capacity of the furnace was from 200 to 270 lb. per hr. Usually the furnace was in the best operating condition at the time it had to be shut down.

culty developed at points near the oil burners, as in preheating the temperature in these regions was necessarily higher than the intermediate zones. The temperature of the various zones, however, were quickly equalized and no trouble was encountered during the first few tests in the furnace, the combustion tube being clean at the end of the test; in later tests, however, after some dust had collected in crevices of the tube, the overheating at the burners caused some slagging between the dust and fireclay, thus developing starting points for accretions.[7] It is not thought that this would cause any trouble in practice for, after the furnace is in operation, it will continue so for a considerable time. In this experimental work, the operations were necessarily short and at infrequent intervals, which meant repeated heating of the furnace with consequent trouble from slagging.

The gases and fine dust were taken from the furnace into the flues through four openings equally spaced around the base of the stack. The flue led first into a settling box, in which the rate of flow of the gases was reduced and screens prevented the channeling of the currents. From this settler, the gases passed through a small Cottrell precipitator for final cleaning. The cleaning was very effective, though this end of the operation was given but little attention. The Cottrell equipment contained four 10-in. tubes 16 ft. long which were thoroughly grounded. In the center of these 10-in. pipes, and connected with the 50,000-volt line, were suspended, on insulators, ½-in. pipes fitted with four kifen edges at right angles to one another. The 400-volt alternating current was stepped up to 50,000 volts and rectified by a Kenetron.

The flotation concentrate used in the furnace was a complex sulfide containing 31.4 per cent. sulfur, 44.3 per cent. zinc, 11.6 per cent. iron. The results of the roasting of this material and conditions existing during the roast are given in Table 1. These show a minimum sulfur content in the roasted product of 2.2 per cent. and 3.5 per cent. for an afternoon period after the furnace had been adjusted to best running conditions. Other tests gave continuous results of slightly over 2 per cent. sulfur.

Tables 2, 3, and 4 show the forms in which the sulfur existed in the roasted product. The particular point of interest in these results is that the sulfur existed largely as sulfate and the quantity as sulfide was small. Table 2 shows the per cent. of SO_2 in the gas corresponding to the roasted ore samples. It is evident that the concentration of gas had no effect in preventing the completeness of the roast; *i. e.*, the sulfur is not higher in roasted products produced in higher SO_2 concentration.

[7] In a large furnace, described later, provision was made for cleaning the furnace, should that be required. It is not probable that in roasting zinc concentrate accretions will be a serious matter, but in roasting copper concentrate high in iron, trouble would develop with ordinary fireclay refractory parts. These would be avoided in large part by the use of a chromite or carborundum interior lining and combustion tube.

Table 2.—*Log of SO_2 in Gases and Corresponding Sulfur Content of Calcines*

(These results are from the run covered by Table 1, Aug. 23, 1916)

Time	Per Cent. SO_2 in Gas	Hopper Sample		Flue Sample	
		Total S, Per Cent.	Sulfate S, Per Cent.	Total S, Per Cent.	Sulfate S, Per Cent.
A.M.					
9.25	3.0				
9.40	3.4				
9.50	4.8				
9.55	5.2	7.0	2.77	5.4	2.22
10.10	5.2				
10.25	5.3	7.1		3.5	
10.55	5.1	7.4	2.06	4.9	2.38
11.10	6.9				
11.30	5.3	7.8		5.5	
11.45	3.0				
12.0	5.3	8.0		5.4	
P.M.					
12.12					
12.30					
12.45		5.1		5.0	
1.05	7.5				
1.15	6.8	7.0		5.0	
1.30	6.8				
1.45	5.6	6.6		4.8	
2.00	5.5	5.9	1.66	4.4	4.07
2.15	5.2	5.4		3.8	
2.30	3.8	1.8			
2.45	3.9	2.5		2.2	
3.00	4.1	2.3	1.45	3.1	2.96
3.15		3.3		3.5	
3.30	3.2	4.3	2.23	3.93	3.8
3.45	5.9	4.1		3.4	
4.15	4.5				
4.20	4.5				
4.30		4.3	1.95	3.78	3.7

Note.—Decreased sulfur content of calcines in the afternoon results from the higher furnace temperatures, as shown by Table 1.

TABLE 3.—*Screen Analyses and Sulfur Content of Roasted Product*
(Run of May 22, 1916)

Screen Test			Analysis			Sulfate S / Total S
Mesh		Per Cent.	Total S, Per Cent.	Sulfate S, Per Cent.	Sulfide S, Per Cent.	
Through	On					
General hopper sample, 287 lb., or 44.1 per cent. of total calcines						
	40	0.3				
40	60	0.6				
60	80	6.3				
80	100	6.2				
100	120	11.4	7.76	1.89	5.87	24.3
120	150	8.0				
150	200	11.7	5.02	2.84	2.18	56.5
200		55.5	2.63	1.87	0.76	71.1
Original sample			4.53	1.83	2.70	24.8
General flue sample, 113 lb., or 17.4 per cent. of total calcines						
	40	tr.				
40	60	0.5				
60	80	1.0				
80	100	1.8				
100	120	4.1	8.08	4.32	3.76	53.4
120	150	4.2				
150	200	6.7	7.54	4.57	2.97	60.6
200		81.7	6.03	4.92	1.11	81.6
Original sample			6.11	4.90	1.21	80.2
General settler sample, 185 lb. or 28 per cent. of total calcines						
	40	0.1				
40	60	0.1				
60	80	0.6				
80	100	1.0				
100	120	4.4	9.71	3.74	5.97	38.5
120	150	1.4				
150	200	5.6	8.63	4.00	4.63	46.3
200		86.8	6.05	5.30	0.75	87.7
Original sample			6.46	5.06	1.40	78.2
General precipitator sample, 64 lb. or 9.8 per cent. of total calcines						
	40	0.6				
40	60	0.2				
60	80	0.2				
80	200	0.2				
200		98.8	6.99	6.65	0.34	95.1
Original sample			7.18	6.85	0.33	95.4

NOTE.—During this run the SO_2 content of the gas in the furnace was fairly constant at 9 to 9.5 per cent. during the greater part of the run.

Hopper sample is calcine collected from the hoppers of the furnace; flue sample is calcine cleaned from the horizontal flue leading to the settler; settler sample is calcine taken from the settler; precipitator sample is calcine taken from the Cottrell precipitator. The coarsest material was from the hopper and the finest from the precipitator.

TABLE 4.—*Screen Analyses and Sulfur Content of Roasted Product*
(Run of Aug. 23, 1916; these results are those covered by Table 1)

Screen Test			Analysis			Sulfate S / Total S
Mesh		Per Cent.	Total S, Per Cent.	Sulfate S, Per Cent.	Sulfide S, Per Cent.	
Through	On					
General hopper sample						
	40	0.9				
40	60	1.6				
60	80	8.9				
80	100	8.1				
100	120	9.3	8.7	1.74	7.0	20.0
120	150	11.5				
150	200	10.6	6.2	2.31	3.9	37.3
200		49.1	3.9	2.88	1.0	73.8
Original sample			5.8	2.35	3.4	40.5
General flue sample						
	40	0.4				
40	60	0.2				
60	80	0.8				
80	100	1.7				
100	120	2.3	9.6	3.17	6.4	33.0
120	150	4.0				
150	200	4.4	8.3	3.41	4.9	41.1
200		86.2	5.6	4.8	0.8	85.7
Original sample			5.9	4.58	1.3	77.6
General settler sample						
	40	0.8				
40	60	0.2				
60	80	0.6				
80	100	1.2				
100	120	1.2	9.0	2.0	7.0	22.2
120	150	2.8				
150	200	10.2	5.7	2.99	2.7	52.6
200		83.0	5.1	4.29	0.8	84.2
Original sample			5.5	4.08	1.4	74.2
General precipitator sample						
40	200	0.6				
200		99.4	6.0	5.84	0.2	97.3
Original sample			6.0	5.89	0.1	98.2

Tables 3 and 4 show that the sulfur exists in the roasted product as sulfide and sulfate, and that the sulfate sulfur is predominant in the fine ore. This is shown not only by the general samples, of which the hopper samples are the coarsest and the precipitator the finest, but also by the screen analysis of the roasted products. High sulfide sulfur is present

only in coarse material, which in total amount is insignificant in flotation concentrate. The total sulfur is highest, in general, in the finest product, but consists largely of sulfate sulfur. Work that cannot be detailed here reveals that this sulfate sulfur is not the result of an incomplete roast in the furnace, but results from a resulfatization of the roasted ore. This resulfatization is due to the relation between partial pressures of SO_2 and SO_3 and the temperature existing in the lower part of the furnace, in the settler, and in the precipitator. Generally, the partial pressure of the sulfur gases is such that no resulfatization of the calcine can take place if the furnace temperature is between 900° and 1000° C. But when this temperature falls to about 800° and below at the flues, the rapid resulfatization of the ore commences. For example, it will be noted that in Tables 3 and 4, the minus 200-mesh material of the hopper samples, *i. e.*, material separated from the furnace at high temperature and immediately cooled, is much lower in total sulfur, as well as sulfate sulfur, than material of the same size from the flue, settler, or precipitator samples, which were subject to the lowering critical temperatures in the presence of sulfating gas. When the aim of the roasting is a practically complete desulfurization, the furnace must be run hot and the calcines and gas rapidly cooled, or separated from each other as soon as they leave the furnace. If the roasting is carried out as a preliminary for sulfuric-acid leaching, as in the electrolytic-zinc process, the sulfating action of the furnace may be used to any desirable degree up to its maximum.

The Proposed East St. Louis Furnace

An increase in height was provided for in the design of the 12-ton furnace it was planned to build at East St. Louis, but which was not completed because of the conditions brought about by the war. Fig. 6 shows that the combustion tube is set to one side instead of concentrically with the downtake. With the concentric combustion tube, it was necessary to place the furnace on posts to provide space for feed and air connections and for repairs. It was also difficult to make pyrometer and air connections from the outside to the combustion tube, at intervals throughout the height, and to provide support for the combustion tube. To overcome these objections, the side combustion tube was designed.

Air and Feed Arrangement

Provision was made for bringing all the air for the roasting from the stoves through the mixer, as in the smaller furnace, or for splitting the current and having a part of the air take this path and the remainder enter the combustion tube near the top of the injector nozzle. Pipe connections to hot- and cold-air sources were placed at intervals along the combustion tube, thus providing for an absolute control of the

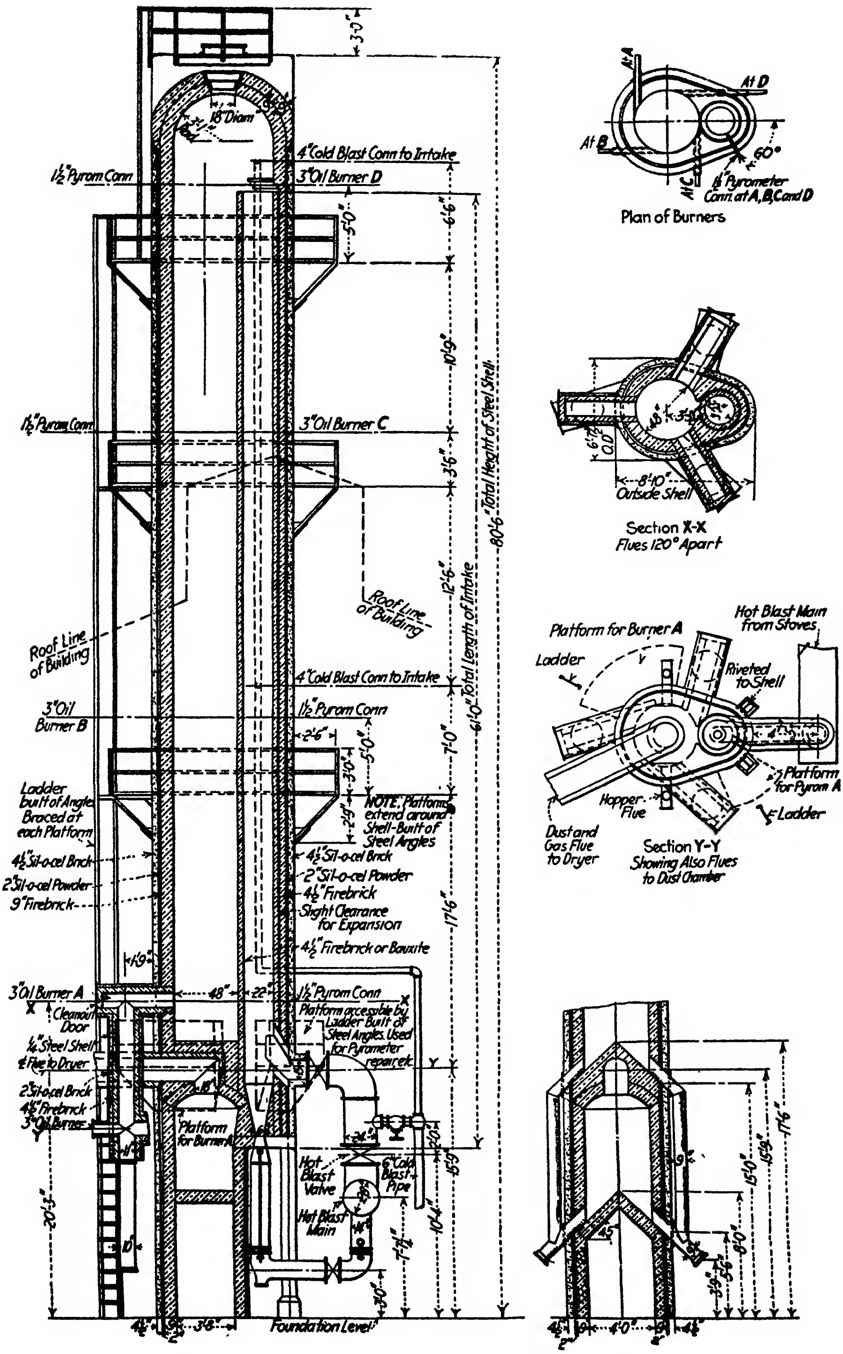

FIG. 6.—PROPOSED PLAN OF 12-TON FURNACE.

temperature in this tube; Fig. 7 illustrates this arrangement of the ore and air feed connections.

Feeder

As in the smaller furnace, a screw conveyor takes the ore from the bottom of the feed hopper to a pipe immediately above a compressed-air

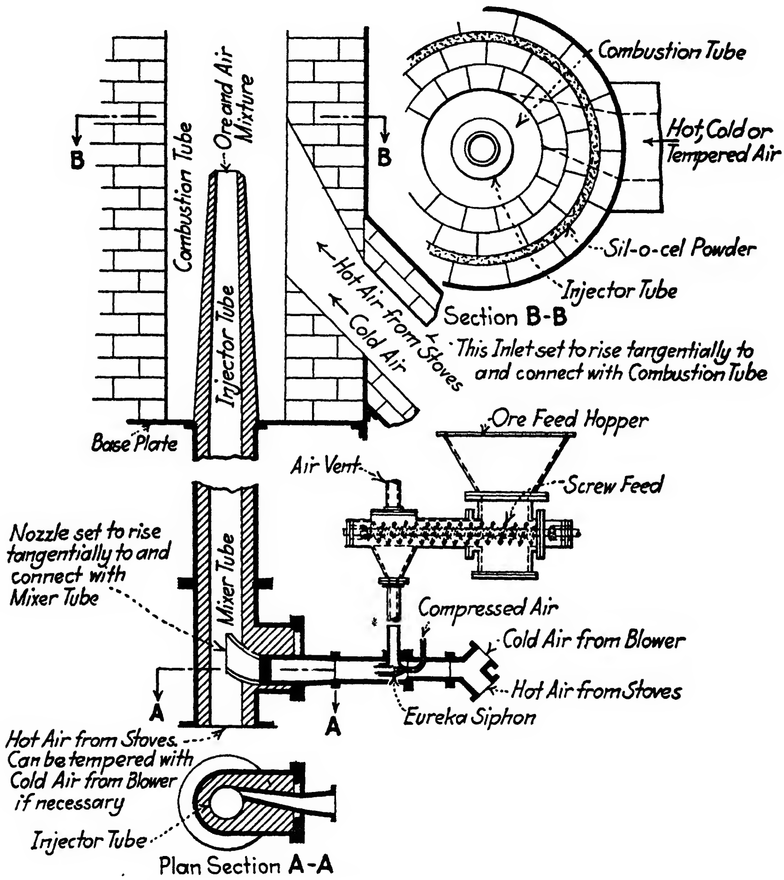

FIG. 7.—FEEDER AND ARRANGEMENT OF 12-TON FURNACE.

injector. The injector was changed considerably from that of the smaller feeder, in order to reduce the amount of compressed air necessary for injection purposes. As shown, the compressed-air nozzle blows directly through a throat, or Eureka siphon, carrying the ore with it and delivering it into a curent of low-pressure air coming from hot or cold sources, or both, by which it is carried forward into the mixer.

Experiments indicate that not to exceed 20 cu. ft. of free air compressed to 30 lb. will be necessary for injecting 1 lb. of ore as against 10

cu. ft. of free air compressed to 60 lb. in the feeder used on the small furnace.

The delivery pipe from the feeder was to be connected to the mixer pipe by the tangential and rising connection that was used on the smaller furnace. The same principle was also to be used in connecting the excess-air pipe into the combustion tube.

Settler

The bottom, or base, plate of the combustion tube was to be raised about 10 ft. from the floor line, to provide for feeder and air connections. The space opposite these connections in the base of the downtake was to be used for the settling chambers for the roasted ore. Accordingly provision was made for the removal of the coarse product from above a bulkhead in the downtake at a point opposite the injector nozzle. The fines and gas were to be taken off, somewhat above this, through three radially placed flues, which flues in turn entered tangentially a settling chamber placed beneath the bulkhead just mentioned. This method of entry was to provide a circular or centrifugal motion for settling the dust. The gases and remaining dust were to be taken off through a flue passing upward and outward through the bulkhead, thence to the Cottrell precipitator.

Heating the Air

There are insufficient data as to how much of the air must be heated and to what temperature heating should be carried for the most efficient operation of the furnace. The effect of heated air on the behavior of the furnace and the ignition has been discussed and it is obvious that one of four methods must be used.

1. Heating all the air and passing all of it through the mixer tube and into the furnace with the ore; this will require large stove construction and will not allow air changes in various parts of the furnace, as will be desirable for proper control.

2. Heating all the air and passing only a part of it into the furnace through the mixer, the remainder to be introduced into the combustion tube at various points; this method is not desirable as the heat is needed in the bottom of the furnace for heating the ore and bringing about early ignition.

3. Heating none of the air; indications are that this will not be possible, as already explained.

4. Heating a part of the air (say one-fifth), which will be passed into the furnace with the ore through the mixer, the remainder of the air to be admitted cold at points throughout the height of the furnace; this method will make all the stove heat available for ignition and for holding down the combustion zone, and will permit the use of cold air for combustion and temperature control of the top of the furnace. Of course, the

stoves should be of ample capacity and of such construction as to permit changing the temperature and amount of air going into any part of the furnace as may be found necessary.

Under the first condition, assuming that 300° C. is necessary for mixer temperature, the air in a 50-ton furnace will have to be heated to 350° in order to heat the ore, if it is being fed cold. If the ore is taken direct from the dryer, this temperature may be reduced somewhat.

The authors calculate that three stoves of the following dimensions will readily take care of a 50-ton furnace: 1060 sq. ft. heating surface, 246 flues, 4 by 4 in. in cross-section, 14 ft. long, and 3¼-in. walls; total height allowing for gas and air ports, foundation and dome about 25 ft.; diameter about 12 ft.; cross-section of combustion chamber 12 sq. ft.

Under the fourth condition, which seems the most rational, such stoves would be more than ample, but not necessarily inefficient, and would provide for emergencies where the heating of all the air was necessary. The ratio of fuel necessary for heating all the air to 250° to that necessary for heating one-fifth to 600° is about as 2.5 is to 1, which is quite a saving in favor of the fractional heating.

Drying the Ore

It is obvious that the feed for this type of furnace must be dry, or it will not pass the feeder and injector. It is likely that most of the concentrate delivered at the roasting plant would have to be dried, so it was planned to do this drying with the waste heat in the gases leaving the furnace, by circulating them beneath the hearth of an ordinary kiln dryer.

That there is sufficient waste heat available for this purpose is readily shown. In the experimental furnace, the gas left the furnace at 800° C. under conditions of best roasting. The volume of this gas (measured under standard conditions) was approximately 50 cu. ft. per lb. of ore roasted and was made up of about 8 per cent. sulfur dioxide; 10 per cent. oxygen, and 82 per cent. nitrogen.

Assuming that these conditions are obtained in a 50-ton furnace:

50 tons per day = 69.5 lb. or 31.5 kg. per min.
69.5 lb. will produce 3475 cu. ft. per min. of gas.
8.0 per cent. of 3475 = 278 cu. ft. SO_2 = 22.7 kg. per min.
10.0 per cent. of 3475 = 347.5 cu. ft. O_2 = 14.1 kg. per min.
82.0 per cent. of 3475 = 2849.5 cu. ft. N_2 = 101.7 kg. per min.

Further, assuming that the gas is lowered in temperature by 400° in passing the drier, the heat available there is:

1. Sulfur dioxide:

Heat capacity[8] at 800° C. is $1 \times 800\ (0.125 + 0.0001 \times 800) = 164$; $164 \times 22.7 = 3722.8$ kg.-cal.

[8] J. W. Richards: *Loc. cit.*, 96.

Heat capacity at 400° C.

$$66 \times 22.7 = 1498.2 \text{ kg.-cal.}$$

Heat available from SO_2 = 2224.6 kg.-cal.

2. Oxygen:

Heat capacity at 800° C. per kg. = 181 cal.

$$181 \times 14.1 = 2552.1 \text{ kg.-cal.}$$

Heat capacity at 400° C. per kg. = 88 cal.

$$88 \times 14.1 = 1240.8 \text{ kg.-cal.}$$

Heat available from oxygen = 1311.3 kg.-cal.

3. Nitrogen:

Heat capacity at 800° C. per kg. = 207 cal.

$$207 \times 101.7 = 21051.9 \text{ kg.-cal.}$$

Heat capacity at 400° C. per kg. = 100 cal.

$$100 \times 101.7 = 10170.0 \text{ kg.-cal.}$$

Heat available from N_2 = 10881.9 kg.-cal.

Total heat available per minute;

$$2224.6 + 1311.3 + 10881.9 = 14417.8 \text{ kg.-cal.}$$

Assuming 20 per cent. moisture in the ore, it will require 39.3 kg. of moist ore to provide the 31.5 kg. of dry ore. This means that 7.8 kg. of water must be evaporated each minute, and 39.5 kg. of ore must be raised to 200° C.

$7.8 \times 650 = 5070$ kg.-cal. to evaporate H_2O

$31.5 \times 185 \times 0.16 = 932$ kg.-cal. to heat ore

Total .... 6002 kg.-cal. to heat and dry ore.

Heat available in gas = 14417.8 kg.-cal.

Heat required to dry = 6002 kg. cal.

8415.8 kg.-cal. in excess

$\frac{6002 \times 100}{14417.8}$ = 41.6 per cent. efficiency of dryer necessary, which is easily obtainable.

It is, therefore, evident that the necessary heat is available for drying and heating the ore. If this heated ore is fed without cooling to the furnace, the temperature of the air from the stoves may be reduced somewhat from that necessary when cold ore is fed. As this amount of waste heat was actually delivered by the small experimental furnace, it is clear that enough heat would be available for completing the roast and maintaining furnace temperatures. As this was possible with a small furnace with a high radiation factor, it would be more readily accomplished in a larger well-insulated furnace.

The dried ore from the dryer will contain some lumps, formed in the drying, and some coarse particles that will not work well in the feeder; it was planned, therefore, to interpose a vibrating screen between the

dryer and the feed hopper to remove these, insuring a satisfactory feed at all times.

Capacity

The capacity of these furnaces will vary as the square of the diameter of the combustion tube. This is substantiated in the results from the 9-in. and 12-in. combustion tubes used in the experimental furnace, which had capacities of 2.0 and 3.6 tons per 24 hr., respectively. Assuming similar conditions as to ratio of air and ore, and the velocity in the combustion tube, the diameter necessary in the tube of a 50-ton furnace will be 45 in. It may be that for a furnace of this capacity it would be better to use two tubes having a combined area equal to 45 in. diameter, *i. e.*, 32 in. diameter each. Such an arrangement would provide for repairs in feeders, nozzles, and injectors on a part of the furnace without complete shutting down the furnace, with attendant cooling.

Table of Estimated Factors for 50-ton Furnace, Operating under Average Conditions

Assumed capacity per day	50 tons
Net area of upcast tube	1590 sq. in.
Net area of downcast tube	7590 sq. in.
Height from nozzle tip to top of upcast	61 ft.
Capacity of stove, per minute, to heat air from 0° to 350° C	1500 cu. ft.
Total fuel (oil or gas) mainly for heater to furnish per day	B.t.u.
Compressor rating, per minute	1500 cu. ft.
Air pressure for compressor, per square inch	30 lb.
Blower rating (cycloidal) per minute	5000 cu. ft.
Cottrell treater capacity, gas per minute (standard cond.)	4000 cu. ft.
Labor (per shift)	2 men
Power requirements for compressor, blower, dryer, feeder, etc	26 kw.

DISCUSSION

G. E. Dalbey, East Berlin, Conn.—What would be the effect on the formation of sulfates of an increased water vapor content in the roasting gases?

Charles H. Fulton.—I cannot answer that from our experience. The question of the formation of sulfate in the roasting of zinc is mainly one of temperature and the concentration of SO_2 and SO_3 in the gases. We found we could roast almost completely to sulfate if the concentration was kept at the proper point. We, however, did not care to do this because we wished to make a 5 to 6 per cent. SO_2 gas for sulfuric-acid work.

The sulfating of the zinc oxide in the proper concentration of gases goes on very rapidly. There are certain places in the furnace system such as the Cottrell and in a part of the dust chamber in which the roasted

ore is subjected for a considerable length of time to the passage of these gases, SO_2 and SO_3, and in which the zinc was almost completely converted to sulfate.

C. S. WITHERELL, New York, N. Y.—Does the presence of iron have any bearing on that?

CHARLES H. FULTON.—Yes, a very great bearing. There has been some work published on the roasting for zinc-sulfate formation, that does not take into account the presence of iron. But the formation of sulfate undoubtedly is greatly aided by the decomposition of sulfates such as iron—no question about that. It is much easier to roast a zinc blend containing an appreciable proportion of iron to sulfate than is a blend without iron.

ARTHUR S. DWIGHT, New York, N. Y.—Is it not a disadvantage that the final gases, just as they leave the furnace, are in contact with the final product? In other words, the gas with the highest percentage of SO_2 and SO_3 comes in contact with the oxide of zinc, tending to reverse the reaction, and form zinc sulfate again.

CHARLES H. FULTON.—That is a decided disadvantage; the only cure is to make that separation at a temperature above the breaking-down point of the zinc sulfate, which is about 700° C.

ARTHUR S. DWIGHT.—Is not that rather close to the temperature at which the reaction reverses itself?

CHARLES H. FULTON.—It is. That reversal is also a function of the SO_2 and SO_3.

B. M. O'HARRA, Rolla, Mo.—Last year we ran several series of roasting experiments in a small laboratory roaster, roasting ordinary Joplin blende with air that we had enriched with various proportions of oxygen. We ran several series at 850° C., and a few at 800° C., and found that there was very little tendency to form zinc sulfate until the sulfide was completely decomposed. That is, the main body of the ore did not contain very much sulfate until the sulfide was gone; but if this main body of ore, after the zinc sulfide was all oxidized, was left exposed to the SO_2 gases coming from parts of the furnace still containing incompletely roasted ore, zinc sulfate would be formed by sulfatization of zinc oxide. Our roaster gases were considerably richer in SO_2 and SO_3 than those described in this paper.

CHARLES H. FULTON.—The decomposition point is very close to 750° with a concentration of, we will say, 5 per cent. SO_2 gas and with SO_3 present.

KURT STOCK, Fish Creek, Wis.—I believe it will be found almost impossible to decompose the zinc sulfate that forms in the furnace, at least in this roaster. We have always found that decomposition of once formed zinc sulfate cannot be accomplished to any worth while extent. In all the established types of roasters, the current of the gases is contrary to the movement of the ore; in other words, the ore is separated from the gases as rapidly as possible so as to prevent sulfatization In this furnace, the roasting ore moves with the gases, which constantly get richer in SO_2 and SO_3. The solution lies in separating the ore from the gases as quickly as possible to prevent the formation of zinc sulfate, rather than try to decompose it afterwards.

CHARLES H. FULTON.—That is the point. We do not wish to form sulfate so that we need not decompose the sulfate after it is formed, hence we endeavor to prevent the formation of sulfate by making the separation of gas from ore at a sufficiently high temperature so the formation of sulfate does not occur with falling temperature. In this furnace, the main body of the ore drops from the gases into hoppers in the lower part. The only ore that is in contact with the gases is that which is carried over into the dust chamber and into the Cottrell.

G. L. OSTGREN, New York, N. Y.—Approximately how long do the ore particles stay in the furnace proper during the roasting?

CHARLES H. FULTON.—In this 30-ft. furnace, about one minute.

Recovery of Arsenic and Other Constituents from Speiss

CLARENCE P. LINVILLE,* ELIZABETH, N. J.

(New York Meeting, February, 1925)

FULTON[1] says: "Speiss is an artificial arsenide of iron containing smaller amounts of other metals. In constitution it is similar to a matte except that arsenic replaces sulfur." For the purposes of this paper it will be necessary to broaden the definition, and I propose the following: Speiss is an artificial mixture of arsenides, of which arsenide of iron may be taken as a type, but iron may be replaced in part or wholly by other metals (such as copper, nickel, cobalt, lead and zinc) and the arsenic may be replaced in part or wholly by antimony. In addition to antimony and arsenic, speisses often contain sulfur. Speisses usually also contain both silver and gold. Table 1 illustrates the variations that may be encountered.

TABLE 1.—*Speiss Analyses*

	Eureka[a]	Globe[b]	Omaha Leady[b]	Perth Amboy Blast Furnace[b]	Concentrated Nickel Speiss[b]	Concentrated Nickel Speiss[b]	Metals Chemical Co.[c]	Arsenical Copper[b]
Gold, ounces	0.84	0.74	1.4	2.0	2.85	6.68		1.56
Silver, ounces		52.0	84.6	78.0	93.6	157.3	205.8	365.2
Iron, per cent	57.02	33.0	20.9	9.1	1.50	1.9	12.8	0.22
Copper, per cent	1.06	6.24	15.0	12.4	9.4	7.6	0.25	40.9
Lead, per cent	2.18	3.6	12.2	0.2	3.5	0.8		2.2
Nickel, per cent		13.4	8.5	19.18	28.2	20.35	20.8	20.2
Cobalt, per cent			2.5	2.5	5.80	4.55	21.5	
Zinc, per cent	0.07							
Arsenic, per cent	32.95	30.4	30.6	29.00	21.0	27.0	35.6	16.0
Antimony, per cent	0.13	6.7	7.5	11.70	17.3	23.5		12.0
Sulfur, per cent	3.34					6.28		0.8

[a] H. O. Hofman: "Metallurgy of Lead," 385. N. Y., 1918. McGraw-Hill Book Co.

[b] From Perth Amboy Analyses.

[c] Metals Chemical Co., Welland, Ontario.

* Metallurgist, Calco Chemical Co., Bound Brook, N. J.

[1] General Metallurgy, 229. N. Y., 1910. McGraw-Hill Book Co.

Attention is called to the high concentration of gold in some of these samples. Hofman[3] says: "As regards the presence of precious metals the fact is to be noted that speiss retains considerable amounts of gold, whereas very little gold is found in matte. Speiss assays show from a trace to 0.5 oz. gold per ton. The presence of metallic iron in speiss furnishes an explanation for the excess of gold over silver usually found, as iron has a strong affinity for gold."

In some of the analyses given, gold to the extent of 6.5 oz. per ton is shown in speisses having only a small percentage of iron. I am inclined to believe that the explanation is that inasmuch as the concentration of speiss is a process in which the metals are removed in so far as possible by matting them out, the fact that silver forms a sulfide soluble in matte, while gold does not, allows the silver to leave while the gold remains behind in the concentrated speiss.

Without question the problem of speiss treatment has been one of the most difficult that the metallurgist has been called on to solve. It is not the purpose of this paper to record the history of this problem and the various attempts to find a satisfactory solution, but to describe some of the methods that have been used in a period of over 10 years at the Perth Amboy plant of the American Smelting & Refining Co. If it were not for the presence of gold and silver, most smelter men would be content to have their speisses go to the slag dump, after a preliminary treatment for recovering a portion of their lead and copper contents. Concentration processes for the removal of copper, lead, and silver can be profitably worked, but the problem begins when concentration can be carried no further, yet the concentrated speiss still contains considerable quantities of both silver and gold. The presence of nickel, cobalt, and antimony add greatly to the difficulty of further treatment.

In order that the different points may be better understood I am going to consider the treatment of a type of speiss such as we have had to work with, showing the following analysis:

Gold, oz. per ton	0.76	Cobalt, per cent	1.8
Silver, oz. per ton	201.00	Arsenic, per cent	18.7
Lead, per cent	21.4	Antimony, per cent	4.6
Copper, per cent	30.1	Sulfur, per cent	3.4
Iron, per cent	10.0	Zinc, etc., per cent	2.1
Nickel, per cent	7.3		

The most satisfactory method for concentrating such a speiss that we found was to crush it to -1 in., mix with about 20 per cent. of its weight of brimstone by shoveling the two together, then charge on the sloping hearth of an oil-fired reverberatory furnace having a magnesite floor for the sloping hearth. The fusion is conducted rapidly so that the molten

[3] "Metallurgy of Lead," 386. N. Y., 1918. McGraw-Hill Book Co.

matte and new speiss formed run into the body of the furnace, where they are allowed to collect until sufficient is present to warrant tapping into pots. While probably good results could have been obtained by the use of a settler for separating the matte and speiss, we used nothing but hand slag pots. These were filled and allowed to cool; when cool the buttons were broken and the speiss separated from the matte.

The sulfur efficiency is very high, from 70 to 80 per cent. of the sulfur used being found in the matte and speiss produced. There is an indication of some arsenic evolution, but from 90 to 100 per cent. of that present in the original speiss will be found in the final concentrated speiss; the same is true of antimony.

In general the limit of concentration is reached when the concentrated speiss contains about 45 per cent. combined arsenic and antimony. The order of removal of metals from speiss is: lead, copper, iron, cobalt, nickel. We have found it possible to produce, by this method, concentrated speisses having the following analyses:

	No. 1	No. 2	No. 3
Gold, ounces	2.85	6.68	2.66
Silver, ounces	93.6	157.3	104.5
Lead, per cent	3.5	0.8	0.2
Copper, per cent	9.4	7.6	12.8
Iron, per cent	1.5	1.9	
Nickel, per cent	28.2	20.35	31.8
Cobalt, per cent	5.8	4.55	
Arsenic, per cent	21.0	27.0	29.2
Antimony, per cent	17.3	23.5	12.8
Sulfur, per cent		6.28	7.8

In cases where the arsenic and antimony percentage totals nearly 40 per cent. sulfur treatment would cause but little concentration; it is then necessary to reduce the amount of arsenic in relation to the cobalt and nickel present. I have always aimed, in speiss concentration, to have only sufficient arsenic and antimony present in the charge to give a speiss with 30 per cent. total nickel plus cobalt, and 44 per cent. total arsenic plus antimony. In other words, I have endeavored to have the ratio of the sum of arsenic plus antimony to the sum of nickel plus cobalt $^{44}/_{30}$. This can be brought about by mixing raw unconcentrated speisses, or by making up the charge in part or wholly of roasted speiss.

From the type speiss above given, the sulfur requirement will be:

		Per Cent.
Lead	21.4 per cent. × 0.155 =	3.32
Copper	30.1 per cent. × 0.254 =	7.64
Iron	10.0 per cent. × 0.571 =	5.71
		16.67

By smelting with 18 per cent. of its weight of brimstone, I should expect to get 53 per cent., by weight, of new speiss and 65 per cent., by weight, of matte.

Concentrated Speiss		Per Cent. of Total	Matte		Per Cent. of Total
Gold, ounces	1.29	90.0	Gold, ounces	0.120	10.0
Silver, ounces	37.1	12.0	Silver, ounces	335.6	88.0
Copper, per cent	12.05	21.2	Copper, per cent	36.5	78.8
Lead, per cent	4.3	10.7	Lead, per cent	29.4	90.
Iron, per cent	10.0	53.2	Iron, per cent	7.2	47
Nickel, per cent	13.1	95.0	Nickel, per cent	0.56	5.0
Cobalt, per cent	3.0	90.0	Cobalt, per cent	0.28	10.0
Arsenic, per cent	35.2	100.0	Sulfur, per cent	23.00	
Antimony, per cent	8.6	100.0			
Sulfur, per cent	7.2				

This speiss is not sufficiently concentrated, but cannot be improved without the removal of some of its arsenic and antimony.

If it be crushed to −20 mesh and roasted on a mechanical roaster, the arsenic content can be reduced to, say, 17 per cent. and the antimony to, say, 5 per cent. During such a roasting the change in weight is almost negligible, so that except for the reduction in the percentage of arsenic, antimony, and sulfur, the analysis of the roasted material will be the same as of the raw concentrated speiss. If this roasted product is mixed with sulfur and some coal to reduce the oxides, and then fused as before, a new matte and concentrated speiss will be obtained. From 53 tons of first concentrated speiss, mixed with 8 tons of sulfur, there will be obtained:

	26.5 Tons Nickel Speiss	10 Tons Matte
Gold, ounces	2.32	0.68
Silver, ounces	36.40	144.7
Lead, per cent	2.00	17.6
Copper, per cent	10.00	37.35
Iron, per cent	7.00	34.65
Nickel, per cent	25.7	1.25
Cobalt, per cent	5.9	0.55
Arsenic, per cent	34.0	
Antimony, per cent	10.00	
Sulfur, per cent	7.00	23.00

By conducting the roast in connection with settling chambers and bag house, or Cottrell plant, the arsenic eliminated by the roasting may be collected and refined for sale. The amount to be expected would be 18.2 per cent. of 53 tons, or 9.64 tons As., or 12.85 tons As_2O_3. If we assume an 80 per cent. recovery, the product will be 10.28 tons refined white arsenic.

The matte obtained from both concentrations will, of course, be sent to the smelting plant to be worked up in the usual manner. It should

be noted that the nickel and cobalt present will partly follow the copper—part will go to new blast-furnace speiss and part to the slags. The greater part, when smelted on a lead charge where arsenic is present, will be found in the speiss made. The following tabulation gives the results of treating a lot of speiss by sulfur concentration at Perth Amboy.

	Gold, Ounces	Silver, Ounces	Copper, Pounds	Nickel and Cobalt, Pounds
Speiss used, 1,321,389 lb.........	1,575.43	177,014	497,503	181,125
Concentrated speiss, 656,700 lb...	1,213.40	30,194	106,229	164,454
Matte, 752,000 lb...............	362.03	146,871	392,541	15,521

	Per Cent	Total Gold, Per Cent.	Silver, Per Cent.	Copper, Per Cent.	Nickel and Cobalt, Per Cent.
Matte made................	57	23	81.8	78.9	8.56
Speiss made...............	50	77	18.2	21.1	91.44

Concentration has also been carried on by using niter cake and coal, instead of brimstone. This gives a very satisfactory speiss product but, because of the sodium sulfide present, the matte slacks badly on standing, if it gets wet, and heats and ignites spontaneously if piled. The time of fusion was increased because of the necessity of removing great quantities of gaseous products from the fusion.

Speisses made with sulfur were apt to be very free from lead and rather high in iron, while those made with niter cake showed rather high lead and were very much lower in iron content. This is illustrated by the following analyses of products from both methods of operating using the same unconcentrated speiss.

	Speisses						Mattes					
	Concentrated with Sulfur			Concentrated with Niter Cake			Concentrated with Sulfur			Concentrated with Niter Cake		
	1	2	3	1	2	3	1	2	3	1	2	3
Gold, per cent.....		3.10		2.75		2.85		0.30		0.10		0.05
Silver, per cent....		104.9		101.7		93.6		278.2		130.4		217.00
Doré, per cent.....	102.0	108.0	72.5	104.45	96.0	96.45	318.0	278.5	227.5	130.5	217.0	217.05
Lead, per cent.....	1.8	0.6	None	3.14	9.6	3.5	27.2	22.2	17.9	13.6	25.2	19.1
Copper, per cent...	7.6	7.8	6.4	5.15	9.6	9.4	23.6	25.8	26.0	11.7	32.1	33.2
Iron, per cent.....	6.9	6.4	5.2	2.5	0.9	1.5	16.0	18.2	18.8	17.4	5.7	8.1
Nickel, per cent...	26.3			28.5		28.2	3.29			1.56		1.22
Cobalt, per cent...	5.95			5.9		5.8	1.60			0.99		1.58

As the presence of lead in the concentrated speiss gave more trouble in its further treatment than iron, it was considered preferable to concentrate with sulfur. Attention is called to the fact that, in sulfur concentration, as opposed to blast-furnace concentration, only a very small amount of slag is formed, and this is sent back to the blast furnace for

resmelting, hence there is no slag loss of metals to be considered by this method of concentration.

The actual results shown by treating 1220 tons of speiss by sulfur concentration were:

	Gold, Ounces	Silver, Ounces	Copper, Pounds	Nickel, Pounds
Speiss used, 1220 tons	2,158.5	229,930	786,052	278,798
Concentration speiss, 550 tons	1,490.7	55,124	193,201	256,501
Concentration speiss, per cent	69.0	23.9	24.6	91.9
Matte, 780 tons	519.55	174,115	597,442	31,065
Matte, per cent	24.5	75.7	76.0	11.1
Accounted for, per cent	93.5	99.6	100.6	103.0

Treatment of Concentrated Nickel Speiss

The earlier method of treating this material was to roast it as completely as possible, care being taken to regulate the roasting so as to give the maximum solubility of the metals present in concentrated hot sulfuric acid. The roasted product was ball-milled in a Hardinge mill running dry. The finely ground roast was treated with hot concentrated sulfuric acid, in a continuous mechanical sulfating machine, the product leached with hot water, separated from insoluble slime, and the solution treated for the recovery of copper, nickel, cobalt, and excess sulfuric acid. In spite of the best roasting, the product always contained from 16 to 20 per cent. of arsenic, which found its way into the solutions and caused much trouble and expense in its elimination from the cycle. For this reason, we developed the method of soda roasting and leaching out the sodium arsenate previous to sulfating.[3]

If any speiss is finely ground and thoroughly mixed with sufficient soda ash to combine with all the arsenic and sulfur present and a portion of the antimony, and this mixture is given a low-temperature oxidizing roast, all the sulfur is converted into sodium sulfate, all the arsenic to tri-sodium arsenate, and a portion of the antimony to sodium antimoniate, while the metals present are completely converted to oxides. If now the roasted product is leached with water, the soluble sodium sulfate and tri-sodium arsenate dissolve and can be almost completely removed by settling and filtration from the residue of metal oxides and sodium antimoniate, which is insoluble in water.

When attempting to get a high-grade tri-sodium arsenate from such material, we found that the sodium sulfate present was an interfering material, which crystallized with the tri-sodium arsenate. To get rid of sulfur, it was necessary to give a preliminary oxidizing roast; which removed part of the arsenic from the speiss and almost all of the sulfur.

[3] C. P. Linville: Production of Tri-sodium Arsenate from Nickel Speiss. U. S. Patent 1505718.

This roasting is not necessary except for the removal of sulfur, as the arsenic can be completely removed by soda roasting even when large amounts of sulfur are present. To illustrate the possibilities of preliminary roasting on the composition of the speiss the following analyses, from operating, are given:

	Unroasted	Oxidizing Roast	Soda Roast
Gold, ounces	5.0		
Silver, ounces	175.0		
Lead, per cent	1.6		
Copper, per cent	9.3	9.5	7.0
Iron, per cent	5.0		3.6
Nickel, per cent	22.0	19.0	16.1
Cobalt, per cent	3.1		
Arsenic, per cent	23.5	17.0	12.6
Antimony, per cent	20.0		14.7
Sulfur, per cent	6.2	0.7	0.6

After considerable experience we were able to conduct the roasting so that the sulfur content of the product could be kept below 0.3 per cent., and in some cases it was as low as 0.12 per cent.

Roasting was carried out on a 22-ft. Herreshoff furnace with eight hearths. Temperature control is very difficult, as the speiss does not begin to roast until near its melting point. I have seen every floor of the furnace with the unroasted speiss charge melted and partly roasted material floating on top of lakes of molten speiss; this condition was remedied and the furnace brought around to normal by increasing the fire and opening the lower doors to give a large excess of air, without cooling the hearths enough to solidify the molten material, which after a few hours was oxidized and disappeared, having been taken up by the roasted material. The furnace was heated by four oil burners, placed in the doors on the second floor and arranged to direct their flame tangentially, thus giving a whirling flame without danger of overheating the center shaft. The temperature control was by means of a recording Bristol pyrometer, on the hearth above the burners. The actual temperature of the roasting mass is not known, but we aimed to hold the pyrometer readings between 1300° and 1400° F. The capacity of this furnace, when roasting concentrated speiss down to 16 per cent. arsenic and 0.5 per cent. or less sulfur was from 15 to 20 tons per 24 hours.

In the case of the type speiss above given, there are 26.5 tons to be treated. Roasting can be expected to reduce the percentage of arsenic from 33.6 to 16 per cent. and the sulfur from 7.20 to 0.3 per cent. This would mean the elimination of 17.6 per cent. of the weight of the speiss or 4.67 tons of As, equivalent to 6.23 tons of As_2O_3, of which 80 per cent. (or 4.98 tons) should be recoverable as white arsenic.

Samples from this roasted material are tested to determine the amount of soda ash necessary for complete conversion of arsenic to sodium

arsenate by making up roasting-dish charges having different percentages of soda ash. These are roasted in a laboratory muffle furnace, cooled, and weighed portions tested for their percentage of soluble arsenic, using an iodine titration on the water solution from the leached sample. From the results of these tests, the minimum amount of soda ash that will give satisfactory results are computed. Charges were weighed up on the floor, based on the use of sufficient speiss to use one bag (300 lb.) of soda ash, the two shoveled together, and the mixture passed through a Hardinge mill. This was necessary to give the thorough and intimate mixture of speiss and soda ash required to insure good results on the following soda roast. Roast speiss with 16 per cent. arsenic requires from 33 to 36 per cent. of its weight of soda ash. The 26.5 tons of the roasted speiss which we are considering and 8.75 tons soda ash should yield 31.27 tons of soda-roasted material. The loss in weight is largely carbon dioxide from the soda ash. This operation can be carried out very well on a mechanical furnace, such as the Herreshoff used for the first roasting, but a Godfrey single-hearth furnace is much better. We used an oil-fired flat-bottom cupel furnace charging the roast mixture in batches of from 800 to 1000 lb. at a time, which gave a layer of from 4 to 6 in. deep over the furnace floor. With a hot furnace, one man was able to handle two charges on an 8-hr. shift. A good red heat was carried, the charge being thoroughly rabbled every few minutes, care being taken to not overheat it during the early stages of the roast. After the roast is complete and danger of fusion of sodium carbonate no longer exists, the heat can be raised without fritting of the charge to a somewhat higher range.

Production of Tri-sodium Arsenate

A pilot leaching plant was operated for four months, producing 120 tons of tri-sodium arsenate. This comprised a dissolving tank, having live steam for heating and a stirrer, a Schriver diaphragm pump, settling tanks, a Sweetland filter press, and two storage tanks; also a double pan evaporating furnace for concentrating sodium arsenate solution. This pilot plant was unsatisfactory in many ways, but gave the necessary information from which a larger plant could be designed.

The sodium arsenate is extremely soluble, but at the same time much of the insoluble speiss residue is of a colloidal nature, rendering it difficult to settle or filter. The proper method of handling the solution and washing would be to use Dorr thickeners and wash counter-current, drawing the almost saturated clear solution of tri-sodium arsenate from one end, and underflowing completely washed speiss residue from the other. It was found that the solution of tri-sodium arsenate always was slightly colored with copper, even though the reaction was alkaline; this gave a decided green color to the crystals made. This trouble was overcome by using sodium sulfide in the clear solution. The amount

necessary was extremely small, not over 1 or 2 lb. per ton of speiss. The copper could not be removed by adding the sodium sulfide to the mixture in the dissolving tank, but was very efficient when added to the clear solution. The precipitated copper sulfide had to be removed by filtration, but it took considerable time to fill a press. The clarified copper-free solution was run to a storage tank, from which it was fed by gravity to the evaporating pans. The pans were filled and refilled until finally each would be about half full of a heavy syrupy liquid, which was tested by pouring a small sample upon a clean iron plate; if it set up solid within a minute or so, the charge was considered finished and was run out into drums. After standing for about 24 hr., these drums were solid and ready for shipment. The first product obtained solidified in two layers, and analysis showed that there was considerable difference between tops and bottoms, as is shown by the following:

	Tops, Per Cent.	Bottoms, Per Cent.	Tops, Per Cent.	Bottoms, Per Cent.
Na_3AsO_4	57.15	32.30	51.32	44.39
Na_2SO_4	1.23	27.46	2.22	17.28
Na_2CO_3	1.70	11.10	2.17	6.02
H_2O	39.84	29.04		

Trouble from this source was eliminated by attention to the preliminary oxidizing roast. With 16 per cent. arsenic and 0.3 per cent. sulfur, the ratio of sodium sulfate to tri-sodium arsenate is so low that bottoms are not formed. The following analyses are given of fused tri-sodium arsenate made from pre-roasted speiss.

	No. 1, Per Cent.	No. 2, Per Cent.
Na_3AsO_4	51.32	56.18
Na_2SO_4	1.95	1.28
Na_2CO_3	1.25	1.86
H_2O	45.40	40.12
As	18.5	20.30
S	0.44	0.29

The 26.5 tons of roast speiss, after soda roasting, amounts to 31.27 tons; after a water leaching this gives 21.2 tons oxide residue and 21.2 tons of fused tri-sodium arsenate containing about 20 per cent. As. The arsenic is all in the "ic" state. The residue will have a dry analysis about as follows:

		Total
Gold	2.90 oz.	61.56 oz.
Silver	45.50 oz.	965.00 oz.
Lead	2.50%	1,060 lb.
Copper	12.50%	5,300 lb.
Iron	8.70%	3,710 lb.
Arsenic	1.30%	
Antimony	11.70%	4,982 lb.
Nickel	31.30%	13,621 lb.
Cobalt	7.37%	3,127 lb.

The Treatment of Soda-roasted Speiss Residue

The residue is taken, without drying, mixed to as thick a mud as can be handled, and allowed to feed into a mixer where it is mixed cold with 66° sulfuric acid in such excess that, when the mixture is heated to complete the sulfating reaction, the result will be a creamy mass thin enough to flow in a stream from the sulfating tool. This consists of a drum 8 ft. long, and 4 ft. in diameter, closed at the ends, and mounted on wheels so that it can be slowly rotated. The residue-sulfuric acid mixture flows slowly and continuously in at one end, mixes with the bath of hot sulfated material in the drum, and an equal amount of completely sulfated mass flows out at the other end. The operation is continuous. The sulfated material drops into a tall cone-bottom dissolving tank, constantly agitated with air. The free sulfuric acid in the sulfate material is sufficient to keep the solution near the boiling point. The soluble metals, including the antimony, are almost instantly dissolved; On dilution, the antimony slimes out again as a white basic precipitate. The solution carrying most of the insoluble material in suspension overflows from a point near the top of the dissolving tank, and is carried to a settling and washing system. Some heavy unsulfated lumps accumulate in the dissolving tank and must be removed, from time to time, by opening a valve at the bottom of the cone and allowing the heavy material to wash out. This material is returned to process, usually to the feed to the soda-roasting furnace.

The solution carrying slimes of undissolved materials from the speiss is flowed into the center of an 8 ft. cone, from which the clear overflow goes to a 1600 cu. ft. settling tank. The underflow from the cone goes to a second cone, where it is thinned with hot water from boiling-tank steam-coil condensation; the overflow from this cone goes to the dissolving tank, flowing in at the bottom, and the slimes to a settling tank. The plant is practically automatic, being run by one man per shift. This man attends to the oil fire heating the drum, and regulates the acid and slimes feeds, as well as the hot water feed, so that the solution running off from the first cone is maintained at a specific gravity between 1.32 and 1.35.

The overflow from the slime-settling tanks also flows to the dissolving tank. When a settling tank is full of slimes, the stream is turned to a second slimes settler. The handling of the settled slimes has not been successfully accomplished as yet. We believe that they could be dewatered by using a suction filter of the Moore type. The method of handling heretofore used has been to drain as much solution as possible from the tank, and then to stir sufficient ground limestone into the slimes to cause them to set up. The stiff mud is then dug out, loaded on to transfer cars, and sent to the smelting plant. From 90 to 95 per cent. of the copper, iron, nickel, and cobalt will be soluble and will go with the solu-

tion, while the gold, silver, lead, and antimony, as well as the remainder of the copper, nickel, cobalt, and iron will be found in the slimes. Because of the presence of reprecipitated antimony compounds, these slimes are milk white and usually have been designated in the plant as "white mud."

In the case of the type of speiss being treated, we should have 21.2 tons of soda-roasted leached residue, mixed with 90 tons of 66° H_2SO_4 which will yield 4380 cu. ft. of solution, analyzing as follows:

		Solution Contains, Pounds
Specific gravity	1.33	365,710
Free H_2SO_4	33.00%	120,685
Copper	1.29%	4,706
Iron	0.90%	3,314
Nickel	3.62%	13,266
Cobalt	0.82%	3,020
Arsenic	0.13%	510

While the white slimes will amount to 9.9 tons, containing

		Slimes Contain
Gold	6.22 oz. per ton	61.56 oz.
Silver	97.4 oz. per ton	965.00 oz.
Lead	5.35%	1,060 lb.
Antimony	25.20%	4,982 lb.
Arsenic	0.37%	72 lb.
Copper	3.0 %	594 lb.
Iron	2.0 %	396 lb.
Nickel	1.8 %	355 lb.
Cobalt	0.54%	107 lb.

It has been customary to return the white mud residues to the lead blast furnaces, but in view of the very high percentage of antimony it might be profitable to give a sodium-sulfide leach before treating the slimes further for their values.

The solution is handled by first passing through a set of "depositing-out tanks," where lead anodes and copper cathodes are used. Because of the low percentage of arsenic present in the solution, it is possible to plate out the copper with a rather high current efficiency, thus reducing the amount to about 0.1 per cent., returning its sulfuric acid to the solution and giving copper cathodes of such purity that they can be added to the refined copper charges.

The solution is now to be concentrated by boiling in lead-lined tanks, containing heavy lead coils; steam is passed through the coils. A reducing valve on the inlet and steam trap on the outlet holds the pressure in the coils to about 30 lb. Under these conditions a rapid boiling takes place, with a steam consumption of about 1 lb. steam per pound of water.

Evaporation is carried far enough so that the solution will have no corrosive action on iron, about 1.45 specific gravity, and then run out into oil- or coal-fired open cast-iron pans, and evaporated until the specific gravity has reached about 1.65. This is somewhat variable, but should be such that when the pan contents cool, the metallic sulfates present, which are insoluble in cold acid of such strength, will separate out and settle away from the excess acid. After settling in steel receiving tanks, the acid is skimmed off and returns to stock, for use with new acid in the sulfating. Thus, although a large excess of acid is used in the dissolving of the metals, the only acid loss from the system is that which is carried out in combination with iron, nickel, and cobalt, along with some mechanically held by the moist basic sulfates from the settling tanks.

The settling tanks are dug out, and the basic sulfates are dried as completely as possible in a centrifuge, but not washed with water, the amount of acid present not being sufficient to repay the cost of evaporation of wash waters. The result is a reddish-yellow crystalline to powdery mass of mixed basic sulfates of iron, nickel, and cobalt. The crude mixed sulfates obtained would amount to about 36 tons and analyze as follows:

	Per Cent.	Pounds
Copper	0.066	49
Iron	5.76	3,314
Nickel	18.56	13,266
Cobalt	4.22	3,020
Free H_2SO_4	12.00	8,580

Treatment at Perth Amboy has stopped at this point and a large accumulation of mixed basic sulfates is now on hand. The price of nickel is so low that there would be no present profit in its recovery. The rather high percentage of cobalt present in the sulfates would seem to promise a good return however. Plans have been under consideration for treating this material, which may be briefly outlined as follows.

The centrifuged mixed sulfates are to be fed upon the upper hearth of a mechanical roasting furnace, and roasted with careful temperature control so that the iron is oxidized to ferric oxide, without decomposing the other sulfates. It has been found possible, on large scale experiments, to thus oxidize over 90 per cent. of the iron present. The solubility of the nickel and cobalt is improved, so that nickel and cobalt can be more easily leached from the roasted material than from the unroasted basic sulfates. This roasting does three things—it removes all excess sulfuric acid, it converts most of the iron to the insoluble ferric oxide, and it either volatilizes any arsenic present or combines it with the ferric oxide, thus keeping it insoluble when the other metals are dissolved. The roast is then to be leached with hot water, giving a solution containing the nickel, cobalt, and a little copper as well as some unoxidized iron. The

amount of iron, however, is small, and after oxidation with bleach liquor, is precipitated in two stages with powdered limestone. The first stage is an almost complete precipitation, which gives a precipitate low in nickel and cobalt that is returned to the blast furnace for use as iron flux; the second stage is iron precipitate, contaminated more or less with cobalt and nickel, which is used to start precipitation of a new batch, in some cases after adding enough sulfuric acid to redissolve the metals. After complete removal of iron, copper is removed by hydrogen sulfide; if zinc is present this will be removed at the same time.

The solution, which now contains only cobalt, nickel, and some lime salts, will be treated with soda bleach to precipitate the cobalt, which will be settled and filtered from the nickel solution and after purification and burning and grinding will be ready for market. The nickel sulfate solution will be precipitated with lime or soda and the heavy paste of nickel carbonate or hydrate used in an electrolytic nickel circuit, the nickel being plated from the solution by using insoluble anodes. The solution, which becomes rapidly acid under such conditions, has its nickel content kept up and its acid neutralized by the use of the carbonate or hydroxide of nickel above mentioned.

DISCUSSION

Carle R. Hayward, Cambridge, Mass.—What temperatures were used in the roasting of this speiss in the concentration?

C. P. Linville.—I do not know. We used the temperature that did the business. The difference between the melting point and the roasting temperature of speiss is very small. I have seen furnaces run for a considerable time at what we thought was a correct temperature but the speiss came out as raw as when it went in; raising the temperature 50° would give us a roast we did not get before. In some cases, a premature raising of temperature has led to disastrous results; raising the temperature above the melting point before roasting melts the speiss.

The roasting must start at the top of the furnace and progress with the heat, which must be high enough to start the roasting. You must not overheat it until the roasting is far enough along so it cannot fuse down and make your material like a lake. Just what that temperature is I do not know, but we have means of knowing when the furnace is too hot or too cold and the operators get to know about where the temperatures are to be kept.

We regulated the roasting on a big furnace by means of thermocouples on the second hearth placed above the material being roasted. We can regulate it very well by having the men maintain on this pyro-

meter a temperature between 1300° and 1400° F., I do not know what the temperature is down in the hearth, but it is a good strong red heat.

EDWARD F. KERN, New York, N. Y.—A few months ago some tests were run on the roasting of speiss, and we had the same trouble due to melting, but that trouble was overcome by supplying steam during the roasting, which enabled complete oxidation of the speiss, which was then followed by the leaching. In some tests it was found, in the case of speiss that was high in lead, the melting occurred quite readily; whereas for speiss low in lead, but high in copper, iron, and nickel, there was no melting.

On account of the low melting point of most speiss, it was suggested that the molten material be oxidized by a blast of air, similar to converting copper matte. The concentration did not go to metal, but the molten material solidified, and oxidation stopped until we added silica. Complete elimination of arsenic was obtained, provided silica was added to combine with the metal oxides, and all metals were converted into silicates, which may be smelted for copper and marked by usual methods. The arsenic was collected as white oxide.

C. P. LINVILLE.—In the early days of our work, we worked with very high-copper material and I have roasted the same lot of speiss three or four times trying to eliminate arsenic and render the metals acid soluble. We found that with high copper, there was practically no arsenic elimination; but when we eliminated the copper, we were able to get the arsenic down to about 18 per cent. There did seem to be some sort of connection between the amount of copper present and the formation of arsenates in roasting.

G. E. DALBEY, East Berlin, Conn.—Would it be possible to roast the raw high-copper speiss at such a temperature as to decompose all the sulfides and to break up all the sulfates and form oxides of all metals present? The oxide of nickel should be insoluble and would not leach in acid. The other oxides would be soluble in acids and this would be a method of separating nickel from other metals. The textbooks show that by heating sulfates at certain temperatures these sulfates decompose and form oxides.

I roasted a nickel copper matte. The object I was trying to attain was making the oxide of nickel insoluble in sulfurous acid and the copper oxide soluble. I found that I could remove practically all of the copper but about 5 per cent. of the nickel went along in solution with the copper.

C. P. LINVILLE.—The textbooks say that nickel oxide is insoluble in all acids. But I have never seen any speiss roasted under the most severe conditions but what was pretty nearly all rendered soluble in hot

concentrated 66° sulfuric acid. The purer the nickel oxide the better the results; but straight nickel oxide is more difficult to dissolve than oxide mixed with copper. When we started at Perth Amboy, we were roasting material that contained up to 40 per cent. copper; which was why we studied the question of concentration by means of sulfur. The dissolving of that nickel and copper from that high-copper speiss material was a comparatively simple thing. We could do it with dilute solution, even with electrolyte solutions from the tank houses. When we got to making high-nickel speisses we had to use the 66° acid.

Arthur S. Dwight.—Many years ago, when some of us were running smelters out in Colorado, the speiss problem was a very serious one. Many an old smelting works in Colorado, Nevada, and elsewhere had accumulated a big pile of speiss alongside the slag dump. After a few years of experimentation and with better furnace practice, the speiss problem seemed to solve itself. The late August Raht used to say the best way to handle speiss was not to make it. The secret of controlling the making of speiss in the lead blast furnace was proved to be a matter of the adjustment of fuel and mechanical conditions of the furnace charge. In other words, by minimizing the reduction to just the point where it is sufficient to reduce the necessary iron for the sulfur and no more, the making of speiss could be almost entirely avoided.

In 1898, at the plant of the Consolidated Kansas City Smelting & Refining Co., El Paso, Texas, there was a large collection of speiss that was very much in the way. After some experimentation, I found that it was possible to add a certain amount of that speiss to the furnace charge; then by reducing the fuel and substituting speiss, pound for pound, that speiss never showed up down below. In other words, we got rid of our bank of speiss, replaced that many tons of coke, and never saw any speiss after that. It is a matter of the regulation of fuel. But I do not wish to be considered as generalizing too broadly; there are conditions where nickel and cobalt are present and must be recovered in some byproduct where the making of speiss is clearly indicated and I dare say that is the condition that prevails at Perth Amboy.

C. P. Linville.—I think what has been said is perfectly true about the iron speiss, but there are different kinds of speiss. Most of the speiss trouble at Perth Amboy came from the people who discovered the silver ores of the Cobalt Camp. They sent the ores all over the United States and the people who smelted them got speiss, containing nickel, cobalt, and arsenic.

Karl Eilers, New York, N. Y.—It is probably true that in running the lead furnaces with an open charge and relatively poorer reduction, some of that arsenic which otherwise would have gone into speiss was driven off and went out at the top of the furnaces, but when

the refineries commenced charging us with bad faith I began to realize that probably a good deal of this arsenic was more or less dissolved in bullion or matte. A large proportion reached the refineries and accumulated there more and more in residues as the copper went through the refining process. That accumulation is what the author finally had to treat and which came to be such a difficult problem, particularly when we began to receive Cobalt ores.

E. P. Mathewson.—When I took charge of the Monterrey plant of M. Guggenheim's Sons in 1897, I found an accumulation of several thousand tons of speiss. My predecessors had evidently decided that it was cheaper to put speiss on the dump than to smelt it. I, however, thought differently, and smelted it. The resulting bullion was shipped to Perth Amboy for refining. There is no difficulty in separating the iron from the arsenic in speiss. The iron goes into the slag, while most of the arsenic goes into the bullion. This is accomplished by reducing the percentage of fuel on the charge. I have seen arsenic sublimate from the surface of such molten lead bullion when heated in lead refining kettles.

Smelting Copper Concentrates in a Converter

By F. J. Longworth,* Copperhill, Tenn.

(Birmingham Meeting, October, 1924)

For a number of years an intensive study has been made to improve the blast-furnace practice at Copperhill not only as to costs but to provide a good grade of gas for the acid plants. This study took us back to the fundamentals of successful pyrite smelting; namely, a blast furnace working on a clean sulfide ore, free from fines, and the use of quartz high in silica as a flux. In 1919, the quality of the flux was improved and its effect on the metallurgy was very marked. To improve the practice further, it was necessary to work out some method of treatment for the sulfide fines and the siliceous and refractory ores, other than in the blast furnace. A series of milling tests indicated that these products could be successfully treated by differential flotation, and in 1922 plans were made and a flotation plant built.

It was estimated that the flotation plant would deliver to the smelter 40 to 50 tons of concentrates per day; the problem was what to do with these concentrates. It was out of the question to attempt to smelt them in a blast furnace because of the dust losses and because our practice demands a charge free from fines for satisfactory operation. There is no custom smelter in the vicinity to which concentrates may be sold, pending the time when the tonnage will be sufficient to warrant roasters and a reverbatory furnace. Sintering and nodulizing were investigated but neither method fitted into our scheme of metallurgy.

A close study of the converter practice was then made to see if some method could not be evolved to smelt this tonnage of concentrates in a converter without preliminary treatment. At that time, the converter installation consisted of two 12-ft. Great Falls converters, which were handling 12 to 14 per cent. matte. The heat balance of the converters working with 12 to 14 per cent. matte was more than sufficient to smelt the contemplated tonnage of concentrates but the mechanical difficulties of feeding fines into the Great Falls converter made the use of this type of converter impractical.

While there was no opportunity to experiment with the Pierce-Smith converter, equipped with a Garr gun, theoretically it seemed practical

* General Superintendent, Tennessee Copper Co.

to handle concentrates in this type of converter. By means of the Garr gun, the concentrates would be sprayed evenly over the bath of matte with the converter blowing, thereby avoiding the bumping, frothing and explosions that occur when such material is charged by the boat load through the mouth of the converter, when it is turned down. What the dust loss might be was unknown but it was thought that the converter would act as an effectual scrubber and the fines would sinter in passing through the zone of intense heat and could be settled out in adequate chambers and reclaimed.

Accordingly, a 25-ft., 12-ft. diameter Pierce-Smith converter was installed and put in operation on Feb. 1, 1923. This converter is equipped with a close fitting hood and the draft is just sufficient to keep the converter from smoking at the mouth.

From the first, this method of treating concentrates has been a success; from both a mechanical and a metallurgical standpoint it has exceeded expectations. The cycle of operations is the same as a converter working on matte and flux.

No bad effects beeause of charging concentrates, such as frothing, bumping, or boiling, have been noted. With a moisture content of 8 per cent., the concentrates work readily through the Garr gun without visible dusting. If the moisture content is much higher, it is difficult to keep the gun open, the charging is slow, and the material falling close to the gun tends to chill that end of the converter.

The dust loss from the mouth is surprisingly low, probably less than from a roaster, and this dust is as readily settled and reclaimed. The metallurgy is excellent. For over 6 months a recovery of 96 per cent. of the copper from concentrates into blister has been obtained.

At first, the concentrates were carefully mixed with the proper amount of flux to give the required slag but the converter will work just as well if the flux and concentrates are charged separately.

At present, the concentrates are charged about 4 tons at a time, and then the required amount of flux is added after the melt has taken place. The use of concentrates benefits the operations by regulating the temperature and aids in keeping the converter properly lined.

The limit in capacity of the converter in terms of concentrates, has not been reached but approximately as high as one ton of concentrates has been handled for each ton of liquid matte charged and good working conditions have been maintained. On a few occasions the converter has been started with an initial charge of matte and the blow has been maintained for 8 hr. by the use of concentrates and flux alone.

How wide an application this method of treating limited quantities of concentrates may have remains to be seen; certainly, at this place, it is entirely successful.

The following data covers the performance of the converter from Feb. 1, 1923, to June 1, 1924:

CAMPAIGN No. 1—FEB. 1, 1923, TO JULY 15, 1923, INCLUSIVE

Blowing time (converter days)	133.8	
Number of blows	180	
Tons of matte charged	15,323	
Copper assay of matte, per cent		Av. 14.54
Tons of blister made	2,790.37	
Time, in minutes, to blow one ton of copper		70.7
Air used per minute, cubic feet		13,520
Blast pressure, in pounds		14
Air per ton of copper, cubic feet		918,800
Air per ton of iron, cubic feet		228,193
Tons flux used	5,956	
Tons of flux per ton of matte		0.39
Tons of flux per ton of copper		2.13
Tons of flux per ton of iron		0.47
Tons of concentrates treated	5,960	
Copper assay of concentrates, per cent		11.94
Tons of concentrates per ton of matte		0.39
Tons of material charged per converter day		213.5

AVERAGE ASSAY OF CONVERTER SLAG

	PER CENT.		PER CENT.
Cu	1.13	Fe	56.4
S	2.90	Al_2O_3	1.8
SiO_2	20.80	CaO	1.3

CAMPAIGN No. 2—AUG. 1, 1923 TO JUNE 1, 1924 (UNFINISHED)

Blowing time (converter days)	238.7	
Number of blows	302	
Tons of matte charged	24,653	
Copper assay of matte, per cent		Av. 14.48
Tons of blister made	5,118.89	
Time in minutes to blow one ton copper		68
Air used per minute, cubic feet		12,680
Blast pressure, in pounds		13.6
Air per ton of copper, cubic feet		860,350
Air per ton of iron, cubic feet		206,324
Tons of flux used	9,826	
Tons of flux used per ton of matte		0.41
Tons of flux used per ton of copper		1.95
Tons of flux used per ton of iron		0.50
Tons of concentrates treated	13,795	
Tons of concentrates per ton of matte		0.56
Tons of material treated per converter day		205.3

AVERAGE ASSAY OF CONVERTER SLAG

	PER CENT.		PER CENT.
Cu	1.08	Fe	56.0
S	2.40	Al_2O_3	1.1
SiO_2	20.80	CaO	1.1

Application of Pulverized Coal to Copper Refinery Furnaces

BY E. W. STEELE,* NEW YORK, N. Y.

(New York Meeting, February, 1925)

IN THE copper-casting department of a modern electrolytic copper refinery there are two kinds of casting furnaces: the anode, for casting crude copper into anodes for electrolysis; the refined-copper, for casting the cathodes resulting from electrolysis into market shapes, such as ingots, wire bars, and cakes. Both furnaces are reverberatories of practically the same general design and are operated intermittently, putting through a charge normally in 24 hr. The treatment of the copper in the two furnaces is similar, in that oxidation followed by skimming and reduction (poling) is carried on in both; but in the refined-copper furnace, the work must be done with greater care and it is of extreme importance that not the slightest trace of impurity be introduced into the copper.

The furnaces usually hold from 150 to 300 tons of molten copper, which constitutes the daily charge. Except in the case of furnaces in the Lake district, where the concentrates from native-copper ores are charged through the roof, the furnaces are charged through the side doors by charging machines similar to those used in open-hearth steel practice.

In 1916, at the Perth Amboy plant, of the American Smelting & Refining Co., located at Maurer, N. J., a study was made of the possibility of firing the copper refinery furnaces with pulverized coal instead of by hand. The proposed method possessed obvious advantages over hand firing and coal was a much cheaper fuel than oil at that time. However, there were several objections to its use, the principal ones being the possibility of increasing the sulfur content of the refined copper and the additional slag that might be produced from the ash. The increase of the sulfur content of the refined copper was the more serious, as more than 0.002 per cent. sulfur is objectionable. Any increase of the slag would be expensive as the copper in this slag would have to pass again through the entire smelting and refining process.

It was thought that certain modifications in operations and furnace conditions, which will be described later, would overcome these objections so the proposition was discussed with a manufacturer of coal-pulverizing equipment. He was uncertain concerning the use of pulverized coal

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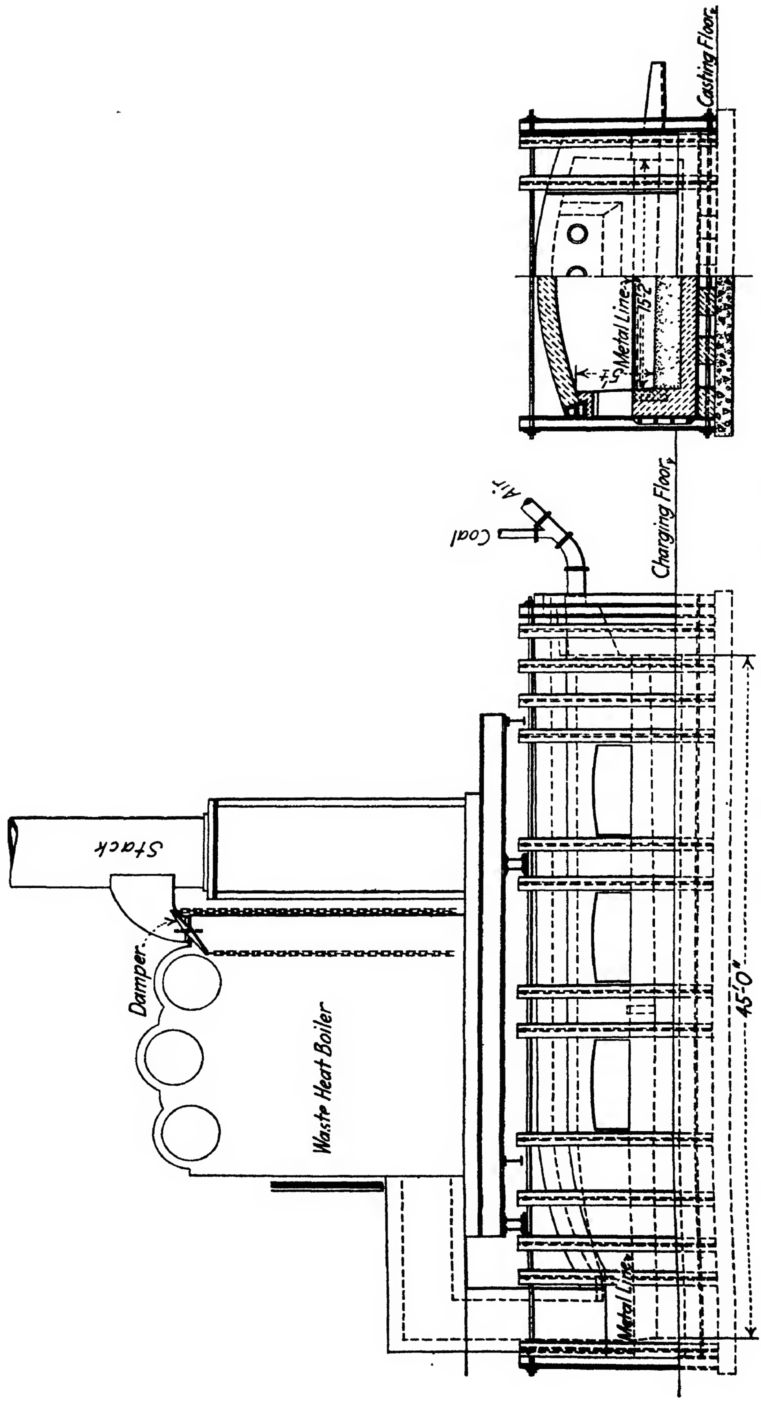

FIG. 1.—COPPER REFINING FURNACE AT PERTH AMBOY PLANT.

under these conditions and suggested that a test be made, offering the use of a pulverizer for this purpose. Inasmuch as the cost of pulverizing and delivering coal to the furnace promised to be considerably less than the labor involved in hand firing, it was decided to make such a test. The furnace selected for the trial had a hearth 15 by 40 ft., and held 350,000 lb. of copper. It was a refined-copper furnace, producing high-conductivity wire bars, therefore, if the application succeeded, there would be no difficulty in applying the new fuel to the anode furnaces.

Equipment Used in Test Run

During the fall of 1916, a screen-type pulverizer was installed and pulverized coal was delivered to a small steel bin near the furnace. Variable-speed screw feeders delivered coal from this bin to the burners in the conventional manner. Unfortunately, there was not sufficient room near the furnace building for all the necessary equipment, therefore the coal was crushed and dried in another part of the plant, using a small dryer that was available. It was thus necessary to deliver the crushed dried coal in bags, a carload at a time. Considerable difficulty was experienced during the operation of the furnace, as the result of delays in delivery and poor condition of the coal, which had absorbed moisture en route.

Results of Test Run

The results of the test run were interesting and favorable. In general, it was found that the solution of the high-sulfur and excess-slag problems was possible. The furnace had been provided with oil-burning equipment, but this was needed only when the coal supply ran short.

In December, 1916, the test run was started. Little trouble was experienced in starting up and fourteen charges were run through using pulverized coal. Although the fuel ratio was high (350 lb. per ton copper) and the time was slow, good copper was produced. In view of the trouble experienced in obtaining a steady supply of well-prepared pulverized coal and considering the experimental nature of the test, the results were promising.

Several different positions of the burners were tried. It was at first considered necessary to utilize the old firebox as a combustion chamber for the pulverized coal so as to trap as much ash as possible and to provide combustion space before the flame should strike the cold copper at the start. It was at once found that best results were obtained with the burners moved up to the old bridge wall, using a short flame in the chamber available at the start of a heat, and gradually increasing the rate of firing as the temperature of the furnace was increased.

Combustion Space Available

The burners were at one time applied through the end wall of the old firebox; this produced excessive heat in the firebox and over the bridge wall but not enough heat where it was needed in the furnace. The burners were then moved about 6 ft. closer and applied directly over the old bridge wall, the results were then much better; in this position the distance from the tip of the burner to the pile of copper in the furnace was approximately 8 ft. Combustion space available was roughly 8 by 10 by 5 ft., or 400 cu. ft.

As the rate of firing must be cut down to accommodate the charging-machine operator, there was perhaps no advantage in having a large combustion space when starting to melt. As soon as charging was completed and the doors were closed, the copper near the burners was partly melted down, thus providing more combustion space and permitting a considerable increase in the firing rate. This rate was increased at intervals of about 15 min. until a maximum was reached, when about 75 per cent. of the cubical contents of the furnace was available as combustion space. The volume of the furnace above the bath line was roughly 2400 cu. ft., 75 per cent. of this is 1800 cu. ft. Firing at the rate of 67 lb. coal per minute gives $1800 \div 67 = 27$ cu. ft. of combustion space per pound of coal burned per minute, which is satisfactory.

There is no question but that the ideal furnace for doing this work would be somewhat different from any of the furnaces used at Perth Amboy, and development work in this regard is yet to be done. Better results could be expected if more combustion space were provided at the start of the melting. A distance of 10 to 12 ft. from burner to charge would be desirable. Another improvement would be to increase the height of the furnace, leaving 2 to 3 ft. of open space above the charge to provide for escape of the products of combustion instead of about 1 ft. as at Perth Amboy.

The conventional constriction at the verb is not necessary when firing with pulverized coal; in fact, a large area at the verb should be provided to lessen the draft-choking effect.

Pulverized-coal Plant Installation

In the spring of 1917, it was decided to proceed with the application of pulverized coal to the copper-casting furnaces, as there was a chance to make a large saving in labor. The necessary equipment was purchased and installed in a building put up for the purpose. In January, 1918, the largest anode furnace, the one nearest the coal plant, was equipped to use pulverized coal. It had a hearth 15 by 45 ft., holding 200 tons of copper. The results were encouraging from the start. In 20 days

the furnace handled twenty charges averaging 185 tons of copper per charge. The coal consumption was slightly less than 200 lb. per ton of copper produced. A few days later, a trial was made to determine the possible speed; eight charges were cast in seven days, which averaged 175 tons each. The coal consumption was less than 200 lb. per ton of copper produced.

These records were made under test conditions, the burners were handled by the department superintendent, and every effort was made to produce the best results. Thus they are comparable to test runs using oil when this work has been done with less than 20 gal. of oil per ton of copper produced. In ordinary operation, the oil consumption varies between 22 and 27 gal. per ton of copper, 25 gal. being about the average figure. With hand firing, the coal consumption was about 250 lb. per ton of copper and six charges cast in seven days was good practice.

Cycle of Operation

The various steps in the cycle of treatment of crude or refined copper in a copper-refining furnace are as follows:

1. After charging, the copper is melted as quickly as possible.
2. When the charge is melted, it is oxidized by blowing air through the bath or flapping with a rabble. This is called "blowing down" or "piping;" the purpose is to oxidize the impurities (mainly sulfur) so that they are volatilized or removed with the slag as oxides.
3. Skimming the slag off the surface of the bath.
4. Poling the copper to reduce the oxygen content. In this operation, green poles, up to 10 in. diameter, are forced down into the copper bath until test buttons, analysis, or microscopic examination show that the excess oxygen has been removed.
5. Tapping the copper from the furnace and pouring into molds. During this period, proper temperature and atmospheric conditions must be carefully maintained.

It is desirable to complete these operations in 24 hr., somewhat as follows: Charging time 2½ hr., melting 8 hr., blowing and skimming 4 hr., poling 3½ hr., tapping 6 hr.

Proper Furnace Conditions and Firing Operations

To meet the objections to firing these furnaces with pulverized coal, provisions were made at the beginning to provide finer coal than is generally used. Experience demonstrated that this was advisable, especially during the poling and tapping period. It was reasoned that if the particles of coal containing sulfur were fine enough the sulfur would be completely oxidized and pass out of the stack with the other gases. It was also thought that with finer grinding a larger percentage of the ash

would be carried through the furnace and out the stack. From experience, it is estimated that under proper draft conditions at least 50 per cent. of the ash is carried out of the stack and there is reason to believe that with fairly fine bituminous coal the particles break up, when subjected to the flame temperature, into extremely fine fragments, most of the resulting ash particles being so small that after passing out of the stack they will float in the air for indefinite periods, perhaps until brought down by rainfall.

Experience at Perth Amboy, covering a period of over a year, showed that some of the conditions necessary to the successful operation of copper-refining furnaces with pulverized coal are:

Sufficient draft and an oxidizing flame during the melting period.

A dependable supply of pulverized coal, which is delivered to the burners under positive and accurate control.

Properly designed burners with an ample supply of air at a suitable pressure.

A good grade of bituminous coal ground to the proper degree of fineness.

Good Draft through Furnace Must Be Maintained

This involves the areas of the reverberatory end, uptake, flue, gas passes through the waste-heat boiler, and the diameter and height of the stack. Lack of draft retards the operations, the copper is fouled, and resultant fuel consumption is excessive. A draft of about 0.2 in. of water in the furnace uptake should be maintained and a velocity of about 2000 ft. per min. through the flues is advisable. Experience has shown that it is necessary to increase the area of gas passages when firing with pulverized coal. Various reasons have been advanced for this. In the case of hand firing, the furnace has been speeded up by increasing the firing rate. In comparison with oil, it is probably necessary to use a larger proportion of air when burning pulverized coal in order to secure quick and complete combustion.

An oxidizing flame is desirable during the melting stage. It should be possible, by providing such a flame, to decrease materially the time required in oxidizing, or blowing down, a charge of copper. This was proved to be true at Perth Amboy but generally it was not possible to provide a highly oxidizing flame there because of restricted flue areas. Interference with building roof trusses etc. made it practically impossible to increase the flue dimensions, therefore it was necessary to decrease the fuel feed instead of increasing the air supply when an attempt was made to produce an oxidizing atmosphere. This resulted in decreased temperature, slower melting speed, and, in the end, an excessive fuel consumption per ton of copper melted. With the Orsat apparatus, it was common to find 17 per cent. $CO_2 + SO_2$ in the gases and only a

trace of oxygen. It is desirable to have 2 to 4 per cent. oxygen in the uptake gases.

An approximation of the volume of gas to be handled from the furnace is as follows:

Furnace capacity, 200 tons copper.

Fuel required, 200 lb. per ton copper; of this amount about 70 per cent. is burned during the melting period of say, 7 hr.

Temperature of exit gases, 2000° F.

Air required at 70° F. to burn 1 lb. of coal is, including necessary excess to provide an oxidizing flame, about 175 cu. ft.

Total fuel consumption for charge would be $200 \times 200 = 40,000$ lb.; 70 per cent. $\times 40,000 \div 7$ hr. $= 4000$ lb. per hr. or 67 lb. per min. maximum rate

$$67 \times 175 = 11,725 \text{ cu. ft. per min. of air required at } 70°\text{F.}$$

The temperature of the exit gases is about 2000° F. At this temperature, the resulting volume will be 54,400 cu. ft. per min. At a velocity of 2000 ft. per min., the uptake and flue area should be 27.2 sq. ft., which is 60 per cent. larger than the areas at Perth Amboy.

The ash problem is also closely related to the draft problem. Probably at least 50 per cent. of the ash is carried out of the stack when conditions are normal; not over 25 per cent. stays in the furnace. This contains silica, which forms a copper silicate and is skimmed off with the slag. The sulfur in the coal that enters as pyrites is probably oxidized to sulfur dioxide and ferric oxide, the former passing out with the other gases and the latter entering the slag with the other inert constituents of the ash. The remaining 25 per cent. of the ash settles in the flue and boiler. This is not a large amount (800 lb. per day, using the above figures and 8 per cent. ash in the coal); but if some of it fuses in the flue, it is difficult to remove and soon chokes the draft and slows down the furnace unless removed.

It is believed that with a uniform velocity through uptake and flue and a design that will eliminate eddy currents, this ash could practically all be carried into the boiler, where it would be cooled immediately and could be easily removed as a dust. Perhaps a better way would be to locate the boiler so that there would be no horizontal flue.

Dependable Supply of Pulverized Coal

A dependable supply of pulverized coal can be provided if the pulverizing plant is correctly designed and has sufficient drying and pulverizing capacity. The feed of coal to the burners must be under control at all times. Practically all the difficulties encountered at Perth Amboy were the result of irregular feeding.

The records made on the first furnace fired, after the test run, were never equalled as a different method of delivering the coal was adopted

and a regular and accurately controllable feed of coal was not obtained. Generally speaking, there are several factors that tend to vary the rate of feeding of pulverized coal. Most of these variations are unnoticeable in a large furnace but any variation will reduce the efficiency of operation. Practically all feeders in use will vary with a change in the moisture content of the coal. They will also feed freshly pulverized coal at a different rate than that which has stood in the bin for some time and has become packed. Under certain conditions, pulverized coal in a bin will partake of the nature of a liquid when it will flow through some feeders at an excessive rate. This difficulty was encountered at Perth Amboy and was not entirely corrected.

The Burners

The burners should be so constructed as to mix thoroughly the coal and air before the mixture enters the furnace and they should not deliver at an excessive velocity. On the other hand, the velocity must always be sufficient to prevent the fire backing up into the burner and overheating it. There must also be enough velocity to prevent any coal being deposited in the burner.

The furnace is never allowed to cool down except for repairs and one burner is generally in use, turned down low, when charging is started. As soon as the first door (nearest the burners) is closed after charging this section of the furnace, the rate of firing is increased as much as possible without interfering with the charging operation through the middle door. By the time the middle door is closed, the copper is beginning to melt near the burners and the firing rate can be again increased. When the third door is closed, it is often possible to top charge through the first door as by that time the copper there is usually flattened down. At any rate, within 2 hr. it is possible to open one of the doors and top charge the desired additional amount.

As soon as the furnace doors are closed and sealed, the burners are adjusted to produce a flame extending practically the entire length of the furnace and, as the temperature is brought up, the rate of firing can be increased. Copper melts at about 1950° F., the flame temperature is about 3000° F., and when the copper is completely melted, it is raised to the desired temperature.

Even before the copper is completely melted, blowing down operations are started on the molten bath. When melting is complete, the rate of firing is reduced and from this time, until the copper is all tapped out, only enough heat to replace that lost through radiation, etc. is required.

During the tapping period, the stack damper is partly closed and it is necessary to maintain the temperature in the furnace at that point which is required for good casting work. The atmosphere in the furnace must be kept as nearly neutral as is consistent with proper combustion, particularly of sulfur.

Three burners were applied to each of the Perth Amboy furnaces but possibly the work could have been done with two. It must be kept in mind, however, that during the tapping period only one burner is needed. If this burner is too large, it will not be possible to turn it down sufficiently and at the same time keep it clear of an accumulation of unburned coal and prevent back firing.

During the melting period, the three burners are delivering 67 lb. of coal per minute (as estimated before) or 22⅓ lb. per min. each. Considerable air is drawn into the furnace by stack draft and the injector action of the burners so that not over 125 cu. ft. of air per pound of coal must be delivered through the burners. A 12-in. diameter burner tip was suitable and at this size, there is $22\frac{1}{3} \times 125 \div 0.785 = 3550$ ft. per min. maximum velocity. As coal will settle out of a stream of air that is moving at less than 1800 ft. per min., a burner of this size will not operate properly at less than half rate—choking and backfiring will result. Figuring as before, 70 per cent. of 40,000 lb. burned while melting, leaves 12,000 lb. to be burned over a period of say 16 hr. or 750 lb. per hr., 12.5 lb. per min., which is slightly more than half the capacity of one of the burners in use.

A pressure of 2 oz. per sq. in. in the air main near the connection to the burner was sufficient at Perth Amboy.

Grade of Bituminous Coal Used

A good grade of bituminous coal should be used in firing copper-refining furnaces. To be specific, the proximate analysis of dry coal should show as follows or better: Volatile matter 36 per cent.; fixed carbon 56 per cent.; ash 8 per cent.; B.t.u. 13,000; sulfur content should not exceed 2 per cent. For best results, the coal should be pulverized so that about 98 per cent. will pass a standard screen of 100 mesh to the square inch and about 88 per cent. should pass 200 mesh. The coal should be dried to contain not over 1 per cent. moisture; otherwise, it is more difficult to pulverize and feed properly.

Comparison with Oil

Practically all the seaboard refineries are now firing with oil, but if the price of oil rises, the use of pulverized coal will no doubt be considered. It was demonstrated that coal can be used in firing the copper-refining furnaces on an equal B.t.u. basis with oil; therefore, when the cost per British thermal unit delivered to the furnace is less with coal than with oil, economy would call for the use of coal as a fuel. When coal is being prepared at the rate of 100 tons per day or over, the cost of this work, including depreciation, upkeep, labor, fuel for drying and interest on the money invested, is approximately one dollar per ton of coal delivered to the burners. The higher cost of handling ash from the flue and boiler

and of smelting the small additional amount of slag produced as against these costs when firing with oil would not exceed 50 cents per ton of coal burned.

With pulverized coal, the upkeep of the furnace brickwork is generally less than with oil; the flame action is not so severe, the heat being more diffused. This is, no doubt, because the combustion of pulverized coal is not so nearly instantaneous as that of oil, for which reason, it is easier to burn oil at a wasteful rate than pulverized coal.

Pulverized Coal at Other Copper-refining Plants

At the present time, the plants of the Michigan Smelting Co., Houghton, Mich., Calumet & Hecla Corpn., Hubbell, Mich., and Anaconda Co., Great Falls, Mont., are equipped to use pulverized coal on copper-refinery furnaces. F. I. Cairns, of the Michigan Smelting Co., states that the company has had no difficulty in using this fuel. The furnaces have been fired with pulverized coal since September, 1921. The coal preferred contains less than 1 per cent. sulfur and 7 per cent. ash. It is pulverized so that 95 per cent. will pass 100 mesh. Other data are as follows: Hearth area, 32 by 15 ft., 350,000 lb. per charge; coal consumption, 400 lb. per ton. Cycle of operations, charging, ½ hr.; melting, 6 hr.; blowing down, 8 hr.; poling, 3 hr.; tapping, 6 hr. The furnaces are equipped with waste-heat boilers and five of them are connected to a 200 by 12 ft. stack. Draft at uptake while melting is 0.10 in. water; 1 per cent. of oxygen is in the uptake gases. Concentrates of native copper ores are treated in the Lake district and results are not comparable with those obtained in electrolytic refinery furnaces.

The Calumet & Hecla smelting works has recently completed a fine coal-pulverizing plant. Firing of two furnaces was started in August, 1924. H. D. Conant states that about 10 years ago the plant began using pulverized coal, a small unit pulverizer being installed to make trials of this fuel for both melting and refining furnaces. The undertaking was successful from the start and the construction of the present pulverizing plant is the outcome. The plant is using a low-ash, low-sulfur coal and no serious difficulty from these factors has been experienced. The coal is ground in air-separator mills until 93 per cent. passes 100 mesh. The full results expected have not been obtained as the company has delayed building a suitable melting furnace until it could form a better idea as to the performance of this fuel.

Frederick Laist, of the Anaconda Copper Mining Co., states that no difficulties were experienced in firing the copper-refinery furnaces at the Great Falls Reduction Works with pulverized coal. Two furnaces were using this fuel from May, 1922, to September, 1923. The hearth dimensions of these furnaces are 13¾ by 36 ft., and they hold 480,000 lb. per charge. The fuel ratio was 294 lb. coal per ton of copper produced. A typical cycle of operations is: Charging, 2½ hr.; melting, 7½ hr.;

blowing down, 6 hr.; poling, 3 hr.; tapping, 4⅔ hr. The furnaces are equipped with waste-heat boilers and stacks 5 ft. in diameter by 142 ft. high. Draft at uptake, while melting, was 0.35 in. of water and approximately 16 per cent. of CO_2 was in the gases. The coal was ground so that 80 per cent. would pass a 200-mesh screen. At present, fuel oil is being used at Great Falls on account of its lower price.

Conclusion

Pulverized coal can be used in copper-refinery furnaces with the same thermal efficiency as oil. A saving of 15 to 20 per cent. usually results when pulverized coal replaces hand firing, using the same grade of coal. Reasonable precautions are necessary for success. A bituminous coal containing not over 8 per cent. ash or 2 per cent. sulfur should be used and it should be well dried and finely pulverized. The furnace, flue, and stack should be proportioned so that a strong draft will be produced through the furnace. The feeders and burners should be correctly designed and the rate of burning must be controlled with intelligence.

When proper conditions, as outlined herein, are attained, there is no question but that pulverized coal is an entirely satisfactory fuel for copper-refinery furnaces.

Acknowledgment

This article was prepared with the assistance and advice of Mr. H. H. Alexander, manager of the Perth Amboy plant during the period covered.

DISCUSSION

Francis R. Pyne, Elizabeth, N. J.—What effect has pulverized coal on the recovery in the waste-heat boiler installation; and what is the evaporation with coal burned in the pulverized form compared to the evaporation by the old method?

E. W. Steele.—Generally speaking, you get a great deal more steam from the boiler when the furnace is fired with coal and oil than with hand-fired coal. The amount of water evaporated per ton of copper treated increases when you burn powdered coal.

Francis R. Pyne.—I know you can get a much higher evaporation than with hand-fired coal, but with pulverized coal when half of the ash goes up the flue and 25 per cent. settles outside, I did not know what the effect would be. It is rather an important point in the expense of running the copper plant.

E. P. Mathewson, New York, N. Y.—In reverberatory copper smelting furnaces, the amount of water evaporated in the waste-heat boiler can be increased up to 75 per cent. of the heat value of the fuel supplied to the firebox of the reverberatory; but that is not efficiency, because the main object of the operation is not evaporating water, but the smelting of ore.

Recent Developments in the Fine Grinding and Treatment of Witwatersrand Ores

By Carl R. Davis,* J. L. Willey,† S. E. T. Ewing,‡ Johannesburg, Transvaal

(New York Meeting, February, 1925)

The first tube-mill on the Rand was put into operation in May, 1904, at the Glen Deep Mine. From that time onwards, tube-mills were added to various plants, although little was known regarding the capacity of a given tube-mill when working on banket ore. Within a few years, however, the so-called standard size (length of shell, 22 ft. 0 in.; diameter, 5 ft. 6 in.) was generally used until the last year or two. Practically the only exceptions were about 30 tube-mills having a length of 16 ft. and a diameter of 6 ft., and a few open-end mills of the roller-supported type. Most of the information obtained during the last 15 years has been obtained with mills of the standard dimensions.

The adoption of the tube-mill as an accessory to the stamp mill was rapid; and where 3 tube-mills were working on the Rand at the end of 1904, 244 were in use seven years later.[1] By 1910, good practice provided 1 tube-mill for 20 stamps of 2000-lb. falling weight. The horsepower of the motors driving the tube-mills had increased from 80 to 100 and then to 125 at this date. Broadly speaking, current practice at that date aimed at a final product of which 60 per cent. was suitable for sand treatment and 40 per cent. for slime. The sand grading was +60 mesh, 6 per cent.; +90 mesh, 25 per cent.; −90 mesh, 69 per cent.; and the slime grading +200 mesh, 2 per cent.; −200 mesh, 98 per cent.

It was recognized comparatively early that the tonnage of −90-mesh product produced by a tube-mill per 24 hr. was a convenient measure of

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[1] W. A. Caldecott, *et al.*: "Text Book of Rand Metallurgical Practice," 2. London, 1912. C. Griffen & Co., Ltd.

relative efficiency of grinding, and this measure has been regularly used since. The battery screening used varied from 15 to 25 mesh per linear inch. Under these conditions, not more than 80 tons of −90-mesh product was produced per tube-mill per 24 hr. The most economical grinding, or pebble, charge was found to be irregular pieces of the banket ore roughly 6 or 7 in., in diameter, picked off the sorting belts, and the weight of the grinding charge represented from 5 to 7 per cent. of the dry weight of the mill feed.

From 1910 onwards when the deep levels of the Far East Rand were opened, to obtain a satisfactory extraction of the gold contents, a much greater degree of comminution of the ore was required. This characteristic became more pronounced as fresh areas were opened farther east, and in two of the mines, then controlled by the Consolidated Mines Selection Co., although situated only a few miles apart, the degree of comminution required to give a satisfactory extraction in the one mine would, in the more easterly mine, give a residue containing approximately double the gold content.

Experimental work demonstrated that only by still finer grinding would a better extraction be obtained. This was carried out to as great a degree as the economic limits of the stamp-tube-mill combination allowed. With the development of the direct tube-milling experiment here described and the economic production of a one-product pulp, which it was found could be successfully handled in the slime and Butters plants, additional work was carried out to determine whether the treatment of this pulp would yield a satisfactory extraction of the gold content. The result of this work showed that a residue containing approximately 25 per cent. less gold could be obtained.

Results Obtained by Increasing Size of Feed to Tube-mills

From 1910, or thereabouts, tube-mill practice on the Rand showed steady improvement. The lines followed were a regular increase in the size of feed, with a corresponding increase in efficiency and a consequent increase in the ratio of tube-mills to stamps. By 1919, when the authors began their practical experimental work, good current practice on the Rand was represented by an output of 125 to 135 tons of −90 mesh per tube-mill per 24 hr. The later milling plants had been designed on a basis of 1 tube-mill to 10 stamps, and the combined 10 stamps and 1 tube-mill were handling approximately 200 tons per 24 hr. The finished product contained 80 to 86 per cent. of −90-mesh of which 55 to 68 per cent. would pass a 200-mesh screen. The power absorbed by the tube-mills had increased considerably so that it was customary to install motors of 150 to 175 hp. to drive them. At the discharge end of the tube-mill, the tendency had been to use progressively larger apertures in the outlet screen and to assist the discharge of material by lifting scoops,

which raise the material to the discharge trunnion. The usual type of discharge screen was provided with ⅞ to 1-in. circular holes. The rounded pebbles passing through this screen consisted almost entirely of the debris of the grinding charge and represented only from ½ to 2 per cent. of the total material fed to the mill. These discharged, or "reject," pebbles were eliminated from the total tube-mill effluent by a small trommel at the outlet end and usually were returned to the stamp-mill bins. The total effluent, less the reject pebbles, was pumped to a sufficient elevation for primary classification in cones, the underflow being returned for distribution over the whole number of tubes through dewatering cones at each tube. The overflow of the primary cones was

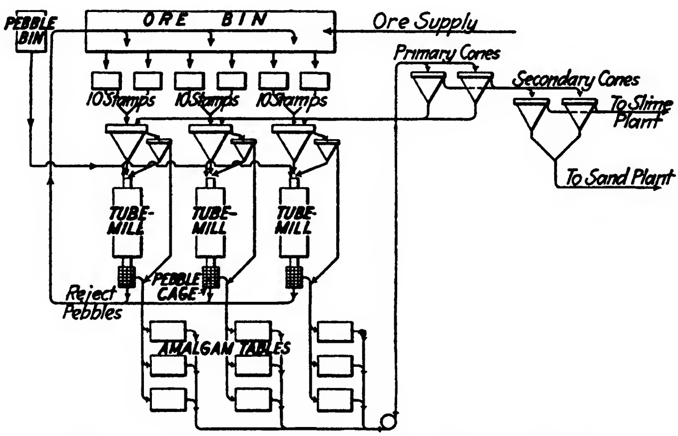


FIG. 1.—ORIGINAL FLOW SHEET AT SPRING MINES.

led to secondary cones for classification into "sand" and "slime." By this date, a proportion of 60 per cent. slime and 40 per cent. sand was being generally arrived at. The flow sheet shown in Fig. 1 was the generally accepted arrangement.

Little doubt existed in the authors' minds, at this date, that the generally improved results obtained were the result, primarily, of the increase in the size of feed to the tube-mills. The best results were obtained by the use of ¾-in. mesh battery screening. In some cases, where the grade of launders between stamp and tube-mill permitted, 1-in. mesh was successfully used. The question naturally arose as to whether a tube-mill fed with ¾-in. product drawn direct by screening from run-of-mine ore or from any form of jaw or gyratory crusher would give as good results as when fed through the same screen from a stamp battery. The proportion of fine material present in a stamp-battery product is considerably larger than that in a crushed product of the same nominal screen; on the other hand, the direct product from a crusher is distinctly more angular than a stamp-mill product, even when the latter is worked

with as large a screen as ¾ or 1 in. Nothing except experiment on a large scale could determine the possibilities opened up.

Experimental work of this nature is costly and apt to interfere with the regular routine running of producing mines, therefore all the more credit is due to the controllers of the Consolidated Mines Selection group of mines (now under the control of the Anglo American Corpn. of South Africa) for providing the necessary funds and encouraging full-scale experimental work to be carried out at two of the mines. As experiments had already shown that on the Rand steel balls as a grinding charge were uneconomical, because of the high cost of imported steel balls, it was decided to confine the experimental work entirely to tube-milling, using the banket pebble as a grinding charge, in accordance with existing practice.

The authors' intentions were to endeavor to ascertain the limiting conditions of size of dry feed that could be economically handled in a standard tube-mill and the design of suitable means for feeding such material into the tube.

Experimental Work at Brakpan Mines

Experimental work was begun in September, 1919, at Brakpan mines. The plant consisted of a separate bin, which was filled by the undersize of a grizzly set, at first, to ¾-in. spacing, from which the ore was drawn in weighed truckloads and deposited in a bin in proximity to a standard size tube-mill. This tube-mill was operated in an independent closed circuit with a primary and a secondary classifying cone. The tonnage fed to the tube-mill was obtained by direct weighing, and the final product, being the overflow of the secondary cone, was regularly sampled for grading analysis. The first difficulty encountered was to get the coarse dry feed with an admixture of only 30 to 35 per cent. of moisture into the tube-mill. The inlet was 9 in. in diameter in the clear, which was the standard size, but various forms of feed hopper, in conjunction with different types of spiral inside the trunnion, failed to give a clear run of the feed without poking or other manual attention. The difficulty was removed by using a hopper of the type shown in Fig. 2, in conjunction with an inlet 12 in. in diameter in the clear.

As the feed material (the desired proportion of grinding pebble and the oversize return from the classifier circuit) is fed on to the sloping back of the hopper, it passes directly into the tube-mill without any manual attention. Hoppers of this design have been successfully used in all recent installations. As the tonnage and grading results with ¾-in. grizzly product showed that the authors' anticipations were in a fair way of realization, the size of the feed was increased to 1-in. grizzly undersize. Under the latter conditions, it soon became obvious that to maintain a good output of −90-mesh product, it would be necessary to increase

the number and area of the holes in the discharge screen, thereby considerably increasing the daily tonnage of reject pebble. The work was continued, using successively larger feed with correspondingly greater reject tonnage, until it was demonstrated that with the undersize of 1½-in. grizzly as feed, a grinding charge of 12 to 15 tons of pebble, and a reject pebble discharge of about 25 tons, a duty of approximately 130 to 140 tons of −90-mesh per 24 hr. could be attained. As approximately 40 per cent. of run-of-mine ore on the Far East Rand deep levels will

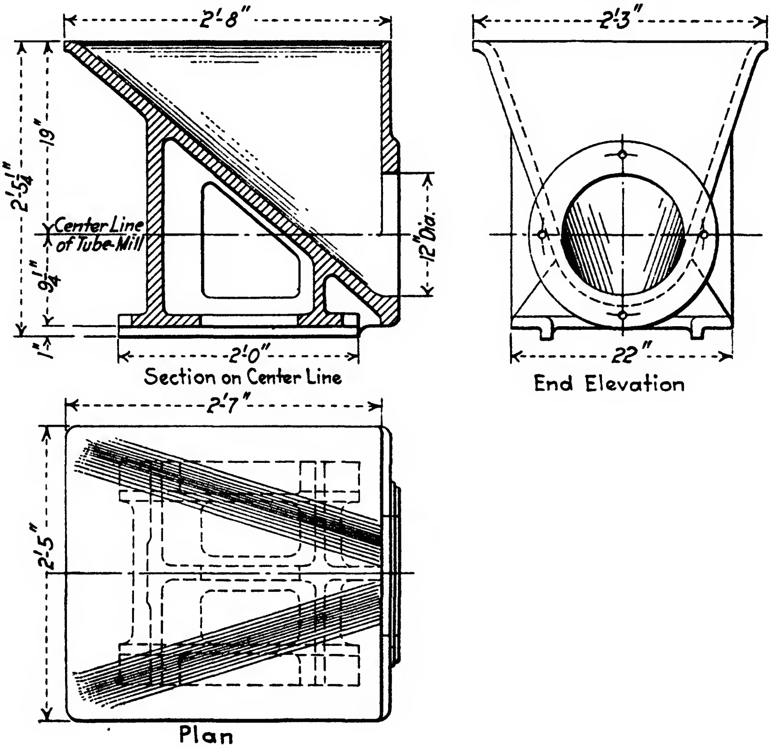


FIG. 2.—NEW FORM OF HOPPER FOR FEEDING TUBE-MILL.

pass a 1½-in. grizzly, it was possible to send a large proportion of run-of-mine ore direct to the tube-mills, which possibility was of sufficient economic importance to warrant further work.

At a comparatively early stage of the work it was found that the use of large, angular ore fragments as the regular tube-mill feed, instead of the ordinary stamp-mill product, resulted in a material modification of the reduction process within the tube-mill. While doubtless considerable reduction is done by the progressive division by fracture of individual pieces into smaller and smaller pieces, there is clear evidence that a greater part than hitherto is taken by the attrition of the angular prom-

inences of the larger pieces. This attrition appears to effect comminution at a rapid rate until the angularities disappear, when the resulting rounded pebbles become an inert constituent of the charge and, if allowed to accumulate, will rapidly reduce the capacity of the mill. The systematic withdrawal of these rounded pebbles on a much larger scale than hitherto practiced, so that they may be broken and again made angular, is therefore the outstanding feature of this process.

Limitations to Use of Banket Pebble as Grinding Charge

Because of the physical difference between the banket ore of the central Rand and the Far East Rand deep levels, a smaller percentage of run-of-mine ore of suitable size and shape is available for the tube-mill grinding charge in the latter area. Tests carried out at the mines of the Anglo American group show that a maximum of 10 per cent. of run-of-mine ore was, in size and shape, suitable for this purpose. In practice, fairly effective tube-milling can be carried out with grinding charges ranging from 3 to 25 per cent. of the total feed. This wide variation connotes different conditions of moisture content of the feed, rate of feed and corresponding grading of discharge, ratio of return oversize to original feed, etc. In the experimental work, it was essential to confine attention to results obtainable with grinding charges well within the limits existing for the supply of suitable pebble. This was fixed, therefore, at a maximum of 20 tons per standard tube-mill per 24 hr.; the best results are attained at about 15 to 16 tons.

The results obtained at this stage led to the consideration of the best methods of supplying ore of the required grading to the tube-mills. It was clear that some form of stage crushing, consisting of ordinary jaw or gyratory breakers, followed by rolls or disk crushers, would give a suitable product, as was suggested by George Denny, for use on these fields. In a paper[2] presented to the South Africa Association of Engineers, in June, 1906, to show the lines intended to be followed for the production of a one-product pulp in which the whole of the values were to be recovered by cyanidation G. A. and H. S. Denny said: "The design of the new plant would be entirely different at almost every point from a plant . . . erected on these fields today. The stamp battery is left out in this design, the principles being stage crushing and stage grinding, the cost of such plant being far cheaper than a stamp battery, while the efficiency has already been decided by work done in other countries."

The form of plant designed by the authors consists of only three stages; viz., primary breaking in gyratory or jaw crushers; tube-milling using large fragments of run-of-mine ore as a grinding medium; cracking

[2] Rand Metallurgical Practice and Recent Innovations. *Proc.* South Africa Assn. of Eng. (1905–06) 11, 239.

reject pebbles in any suitable form of crusher, giving approximately a ½-in. product. This is a much simpler series of operations than that envisaged by G. A. and H. S. Denny in 1906.

The experimental work at Brakpan showed that a line of demarcation could be drawn between what may be described as the old and the new process of tube-milling in terms of the size of feed, and that the actual location of the line was between feeds of −1-in. and +1-in. mesh. Below the line, one would expect in a standard tube-mill, working on Far East Rand ores, an actual production of 130 to 140 tons of −90-mesh product per 24 hr., with a pebble reject varying from ½ to 2 per cent. of the total feed. Above the line, when using a tube-mill of the same dimensions, in order to secure efficient grinding, the required tonnage of reject rises rapidly; in fact, with a −1¾-in. feed, it was advantageous to reject as much as 15 to 20 per cent. of the total feed. Under these latter conditions, a remarkably high percentage of −200-mesh was easily produced and the −90-mesh production rose to the order of 145 to 150 tons per 24 hours.

Two alternatives presented themselves; viz., two-stage crushing, having for its object the production of a −1-in. feed to the tubes, as an improvement on single-stage crushing and stamp-milling to 1-in. mesh; or single-stage crushing prior to tube-milling, followed by secondary crushing, or rather cracking of the reject pebbles.

It was thought that the latter alternative promised the better results. There was no doubt that the considerably increased fineness of the final product shown to be economically obtainable (*i. e.* in terms of horsepower-hours per ton of −90-mesh product), under the new process was due to the coarse and angular nature of the feed. The tonnage of reject pebbles to be crushed is appreciably less than that which would have to pass the secondary crushers under the first system. Further, about 3 per cent. of the total feed could be sorted on the reject-pebble belts and thereby eliminated from the second passage of the reject material through the plant. Having arrived at this conclusion, the question of obtaining the best available product from the primary crushers became one of great importance. It had not been the practice to make special provision for securing an even continuous feed to the primary crushers, therefore experiments were instituted to ascertain the over-all effects obtained by maintaining a full and continuous feed. The first experiments were made with jaw crushers having an hourly capacity of approximately 50 tons of −2½-in. product. Under the conditions existing, it was not possible to get a bin of sufficient capacity to maintain a choked feed for more than a few minutes at a time; results, however, were promising. Later, when applied to a crusher of the gyratory type, it was soon found that the improvement in product was remarkable; as the wear was distributed more evenly over the grinding surface there was an actual economy in

maintenance and although the maximum horsepower required was increased 20 per cent., the total power consumption remained unaltered.

Experimental Plant at Spring Mines

This information having been obtained, it was decided to build a new experimental plant in which run-of-mine ore would be subjected to single-stage crushing only and then fed directly to the tube. The reject pebbles were to be passed directly to a secondary crusher and then fed back to the tube. An experimental plant on these lines was, therefore, erected at Springs Mines in 1920. The flow sheet shown in Fig. 3 illustrates the general arrangement of this plant. A set of 36 by 16-in. rolls cracked the

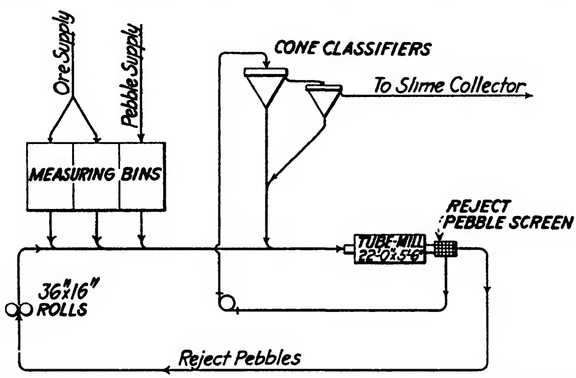


Fig. 3.—Flow sheet of Spring Mines experimental plant.

reject pebbles. The capacity of these rolls was largely in excess of that required by the experiment, but they were used as they were available.

The mill used was a standard 22 ft. 0 in. by 5 ft. 6 in., running at 28 r.p.m. and driven by a 175-hp. motor. The inlet to the mill was 12 in. in diameter and the outlet was 17 in. A lift with arms 4 ft. 3 in. in diameter raised the pulp at the discharge end. The discharge screen was slotted, the slots being 1¼ in. wide and from 3 to 6 in. in length. Standard steel liners of local manufacture were used; their wear was quite normal. The power input to the mill was metered directly.

Two results were clearly demonstrated with this plant: (1) The practicability of direct tube-milling of a much coarser feed than had been attempted in a standard sized tube-mill; (2) the high efficiency, in terms of −90-mesh production, with this size of feed.

During the test, the feed to the mill consisted of a mixture of headgear fines (undersize 1¾-in. grizzly product) and the oversize of the grizzly, which had been passed through gyratory crushers running with a choked feed.

Note.—The tube-milling process here described is subject to the following patents: Union of South Africa 1086 (1921); Southern Rhodesia 1746 (1922); Mexico 21814-1922 (1922); United States 1461977 (1923); Canada, 241888 (1924).

Because of the layout of the experimental plant, in relation to the mine plant, it was not always possible to obtain as high a proportion of the fine material as is actually produced from the mine, and it was often impossible to obtain the supply of properly crushed material so that frequently an excess of oversize had to be milled.

From April 2 to 29, 1921, inclusive, there were fed to the mill 3,016.89 tons, and the actual running time was 489.03 hr. The average figures over the whole run were as follows:

Tons of feed per 24 hr.	135.00
Tons of pebbles per 24 hr.	12.91
Total tons per 24 hr.	147.91
Tons —90-mesh per 24 hr.	144.32

The production of −90 mesh per horsepower per 24 hr. (measured as input to the motor) was 0.834 ton.

GRADING OF TUBE-MILL FEED

Mesh	+2 in.	+1¾ in.	+1⅜ in.	+1¼ in.	+1.05 in.	+0.742 in.	+0.525 in.	+0.263 in.	+60-mesh	+90-mesh	+200-mesh	−200-mesh
Average Grading												
Product, per cent.	12.6	2.2	11.0	6.2	14.2	14.7	10.5	11.0	12.4	1.3	1.3	2.6
Cumulative Grading												
Product, per cent.		14.8	25.8	32.0	46.2	60.9	71.4	82.4	94.8	96.1	97.4	

The average grading of the final pulp was +60-mesh, nil; +90-mesh, 2.3 per cent.; +200-mesh, 35.2 per cent.; −200-mesh, 62.5 per cent.

NOTE.—The amount of −200-mesh in the final product is approximately 15 per cent. less than that attained in later work with Dorr classifiers.

These samples were taken hourly and divided into shift samples for grading.

The following figures relate to a six-day period when the feed to the tube-mill was maintained similar to that which is to be expected from a plant designed for direct tube-milling.

Tons of feed per 24 hr.	144.18
Tons of pebbles per 24 hr.	14.22
Total tons per 24 hr.	158 40
Tons -90-mesh per 24 hr.	151.48

The production of −90 mesh per horsepower per 24 hr. was 0.874 ton.

Total feed of tube-mills, tons	883.83
Actual running time, hours	133.82

GRADING OF TUBE-MILL FEED FOR 6-DAY PERIOD

Average Grading												
Mesh.......	+2 in.	+1¾ in.	+1⅜ in.	+1¼ in.	+1.05 in.	+0.742 in.	+0.525 in.	+0.263 in.	+60 mesh	+90 mesh	+200 mesh	−200-mesh
Product, per cent......	2.1	0.7	4.2	4.9	23.8	18.0	11.3	15.5	14.1	1.4	1.3	2.7
Cumulative Grading												
Product, per cent.....		2.8	7.0	11.9	35.7	53.7	65.0	80.5	94.6	96.0	97.3	

The average of the final pulp was +60-mesh, 0.2 per cent.; +90-mesh, 4.2 per cent.; +200-mesh, 35.2 per cent.; −200-mesh, 60.4 per cent.

The considerable increase in tons crushed per 24 hr. in the second series of tests was undoubtedly due to the lower percentage of +1⅜-in. material present in the original feed.

COMPARISON OF RESULTS OBTAINED BY EXPERIMENT AND IN PRACTICE

In order to compare the foregoing results with the results obtained at Springs Mines under standard combined stamp-mill and tube-mill practice, the average results for the year 1920 are given:

	Stamps	Be-lls	Tons Milled per Unit per 24 Hr.	Per Cent. −90-mesh in Pulp	Tons of −90-mesh Produced, per Horse-power per 24 Hr.
Springs Mines results for year 1920.	10	1	200.0	88.0	0.9025
Average results of 24 days' trial...		1	147.9	97.6	0.834
Average results for 6 days' trial....		1	158.4	95.6	0.874

The test figures just given were obtained by the collaboration of the Consolidated Mines Selection Co. with the Central Mining & Investment Corpn. and the Johannesburg Consolidated Investment Co., every care being taken by the technical representatives of the groups concerned to secure the greatest possible accuracy.

As already stated, the opening of the deeper level mines of the Far East Rand basin had shown that considerably finer grinding was required to obtain a reasonable percentage of extraction than is necessary on the mines of the Central Rand, but the practical limit of fine grinding from the point of view of over-all economy seemed to have been attained on the existing stamp-mill *cum* tube-mill plants with a sand-slime percentage ratio of about 40 to 60, a point at which practice had remained for some years. The Springs Mines experiments at once opened the possibility

of economically reducing the whole output to a slime; *i. e.*, at least to a product capable of treatment in the existing Butters filter plants.

First a Dorr classifier was substituted for the classifying cones— this was the first Dorr classifier installed on the Witwatersrand mines. The Dorr classifier was tried because to procure a fine overflow from the classifying cones (*i. e.*, of the order of 65 per cent. upwards of −200-mesh) an undue percentage of finished product must be returned to the circuit and at the same time the underflow is unduly high in moisture for tube-milling. After the necessary alterations and additions had been made, a pulp suitable for direct treatment in the existing slime plant was sought.

Altogether 18,000 tons of the one-product pulp were produced and treated by direct cyanidation in the slime plant, without amalgamation. The conclusion of the experimental work showed that the following results could be relied on by the new process of tube-milling:

1. Using a tube-mill of standard dimensions with feed subjected to single-stage crushing only, an output of from 145 to 150 tons of −90-mesh per 24 hr. could be obtained, the grading of this product being: +60-mesh, nil; +90-mesh, 1 per cent.; +200-mesh, 27 per cent.; −200-mesh, 72 per cent.

2. That this product is suitable for direct cyanidation as a slime in an ordinary Butters filter plant.

3. That an over-all improvement of at least 0.20 dwt. in the final residue would be attained over the existing treatment, which dealt with 40 per cent. sand and 60 per cent. slime.

4. That the saving in working costs would be approximately 5 pence per ton milled and the saving in residues at least 10 pence per ton milled.

In view of the foregoing results and that extensions to the milling plant at Springs Mines were called for at this time, it was decided that these extensions should take the form of four standard tube-mills to be operated in closed circuit with Dorr classifiers, and that the new plant should produce a one-product pulp for direct cyanidation in the extended slime-Butters plant, without amalgamation. This plant was nearing completion in January, 1922, when the labor upheaval occurred; this was followed by the revolution in March. When operations at the mine were resumed, advantage was taken of the necessary reorganization of personnel to eliminate amalgamation from the existing stamp-mill *cum* tube-mill plant, as the experimental work had shown that amalgamation could be dispensed with in favor of direct cyanidation. Numerous other mines on the Witwatersrand decided, at the same time, to cut out the amalgamation process but, except at Springs Mines, this was effected by the use of corduroy blanketing laid over the existing amalgamating tables.

The elimination of amalgamation at Springs Mines was followed by a slight improvement in extraction and no difficulties or drawbacks have been experienced in this connection during the two years or so that this

method has been in operation. The logical conclusion of this process would be the substitution of a cyanide-solution circuit for the existing water circuit for milling and slime collection, and as soon as an opportunity is afforded, this change will be made.

The original method of precipitation at Springs Mines was by means of the ordinary type of box containing zinc shavings. At the end of 1922, this was changed to zinc-dust precipitation in Merrill presses in combination with the Crowe vacuum process. The savings effected by this are as follows:

	Zinc	KCN 100 Per Cent.	H_2SO_4	Precipitation and Smelting Costs per Ton of Ore Treated
Average for 1921 with extraction boxes	0.202	0.381	0.175	5.908
1923				
January	0.156	0.478	0.319	4.745
February	0.097	0.457	0.141	3.926
March	0.104	0.417	0.126	3.613
April	0.107	0.402	0.111	4.265
May	0.086	0.363	0.071	3.237
June	0.101	0.360	0.062	3.395
July	0.044	0.340	0.058	4.147
August	0.053	0.330	0.042	3.035
September	0.054	0.346	0.036	2.850
October	0.050	0.365	0.033	2.681
November	0.049	0.360	0.027	3.286

In Fig. 1 is shown the original layout at Springs Mines, while the layout of the new section of the plant is shown in Fig. 4; Fig. 5 shows the

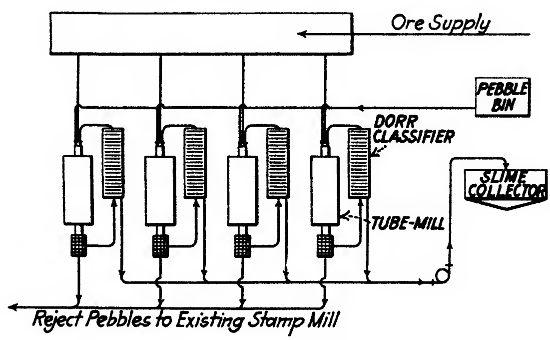


FIG. 4.—FLOW SHEET OF NEW SECTION OF SPRING MINES EXPERIMENTAL PLANT.

arrangement of feed and pebble bins, tube-mill and drive, and Dorr classifier.

It will be noted that the problem of main pulp elevation is simplified to one of elevating slime 25 ft., or so to the slime collectors. This is different to the standard arrangement on the Witwatersrand, which calls

for the elevation of the total tube-mill effluent minus the reject pebbles (½ to 2 per cent. of the total feed) 60 to 70 ft. to the primary cone classifiers—this height is necessary to allow the primary cone underflow to be returned for distribution over a row of 10 to 12 tube-mills. The

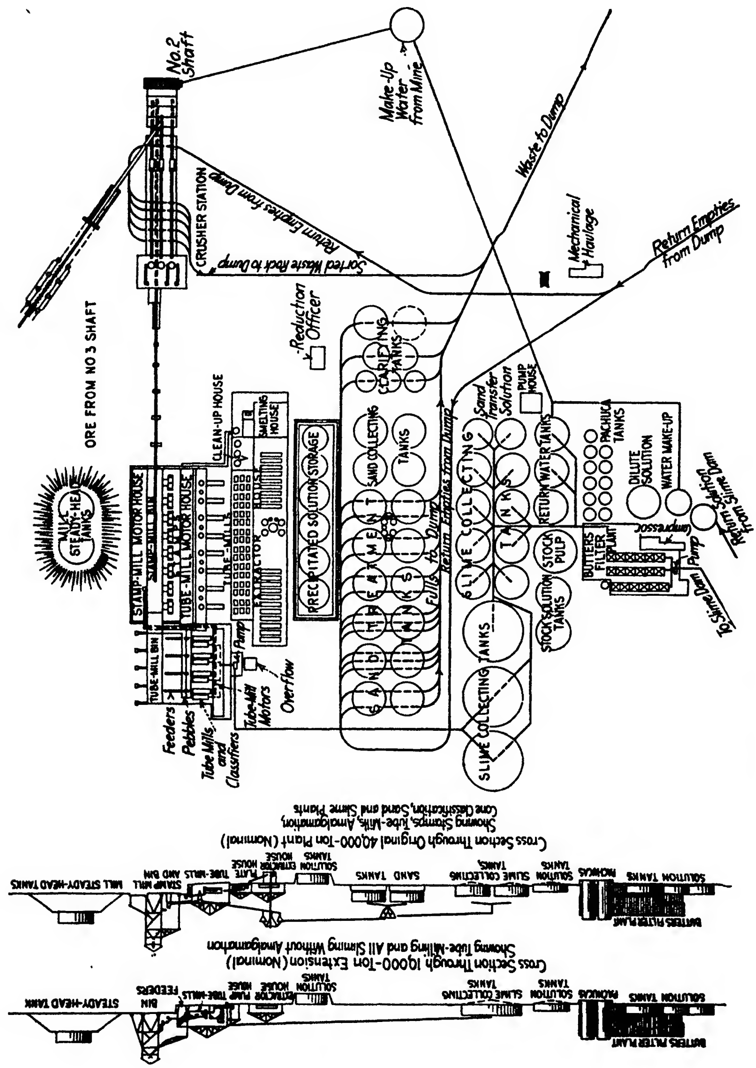


FIG. 5.—ARRANGEMENT OF OLD AND NEW SECTIONS OF SPRING MINES PLANT.

wear and tear of pumps handling such a coarse product to such elevations is excessive, with correspondingly high maintenance and renewal costs.

The substitution of Dorr classifiers in closed circuit with their corresponding tube-mills for the centralized cone classification system has the further advantage that the individual grinding performance of each

tube-mill can be subjected to close and continuous supervision, an extremely important matter that is difficult of attainment with the usual type of plant. As shown in Fig. 5, the feed to the individual tube-mills is carried by a simple belt feed which may be driven at three speeds, the middle speed being sufficient to maintain the normal hourly tonnage required by the tube-mill. One of the other speeds is 10 per cent. above and the third 10 per cent. below this predetermined figure. The feeder is provided with a revolution counter and, provided the ore in the mill bin is properly mixed (*i.e.*, the coarse and fine material are not unduly segregated and the chute openings supplying the feeder are maintained constant) the counted revolutions of the feeder form quite an accurate index of the tonnage fed. It is, of course, necessary to establish a factor for multiplying the counted revolutions; this is obtained in regular practice by comparing the measured tonnage of slime, corrected for moisture, treated in the agitator tanks with the counted revolutions. This method enables the tonnage per tube-mill per shift to be readily ascertained with an accuracy of 3 to 4 per cent.

The results for the month of June, 1923, of the four tube-mills at Springs Mines, working under the new process, are as follows:

Number of working days	26
Number of tube-mills	4
Actual running time	25.875 days
Tonnage produced	15,260
Tons per tube-mill per 24 hr. (calendar time)	146.7
Tons per tube-mill per 24 hr. (running time)	147.4

Average grading of product: +60-mesh, nil; +90-mesh, 2.1 per cent.; +200-mesh, 26.5 per cent.; −200-mesh, 71.4 per cent.

Comparative Figures of Residues Obtained at Springs Mines

	A Dwts. per Ton	B Dwts. per Ton	C Dwts. per Ton
Average	0.62		
January		0.578	0.415
February		0.572	0.434
March		0.574	0.404
April		0.584	0.422
May		0.597	0.497
June		0.542	0.438
July		0.579	0.452
August		0.588	0.483
September		0.545	0.458
October		0.528	0.416
November		0.539	0.440

Column A is original plant when amalgamation was practiced.
Column B is original plant since elimination of amalgamation.
Column C is new plant.

Reduction Costs

The new section is operated in conjunction with the old, and under these conditions it is impossible to allocate costs with complete accuracy. As the result of close consideration of the separation of costs in the two sections, it has been found that a saving of 5 pence per ton milled has been effected.

Running Time

Careful records are kept of the running time on both old and new milling plants. Both plants are operated by the same maintenance and running staffs and consequently the figures disclosed by the records may be taken as a true index of the reliability of the two plants.

The average running times for the period March to December, 1923, inclusive, are as follows: Old plant, 93.389 per cent. of the possible; new plant, 95.751 per cent. of the possible.

Tonnage Capacity of Tube-Mills in Relation to Grading of Product

All work on tube-milling carried out by the authors has been confined to producing a product between somewhat narrow limits of grading; in fact the range has varied only between 97.5 per cent. of −90-mesh, containing 68 per cent. of −200-mesh, and 100 per cent. of −90-mesh, containing 77 to 80 per cent. of −200-mesh. The lower limit is about the coarsest product that can be really satisfactorily treated in the existing Butters filter plants. The upper limit represents about the finest grading that is economically desirable after balancing the lower value of residues against the increased working costs, both of course under our special conditions. The whole practical value of this work is dependent on the nature of the Far East Rand ores from the point of view of the necessity for finer grinding than has hitherto been the practice. No work has been done by the authors to ascertain the output of a tube-mill on the coarser degrees of product that would be desirable on other types of ore. The only guide to the increased output that could be expected with a coarser product, which has been elicited from the authors' work, is that the percentage of diminution in the amount of −200-mesh in the finished product is accompanied by approximately twice that percentage increase in the tonnage output; *e. g.*, reducing the −200-mesh content of the finished product from 77 to 72 per cent. (or 5 per cent.) is accompanied by 10 per cent. additional output per 24 hours.

Bearing in mind that the conditions of the tube-milling here described necessitate running a heavy return circuit, approximately 4 to 1, there is every reason to think that the tube-mill unit now being adopted (6 ft. 6 in. diameter by 20 ft. long) under conditions of comparatively coarse

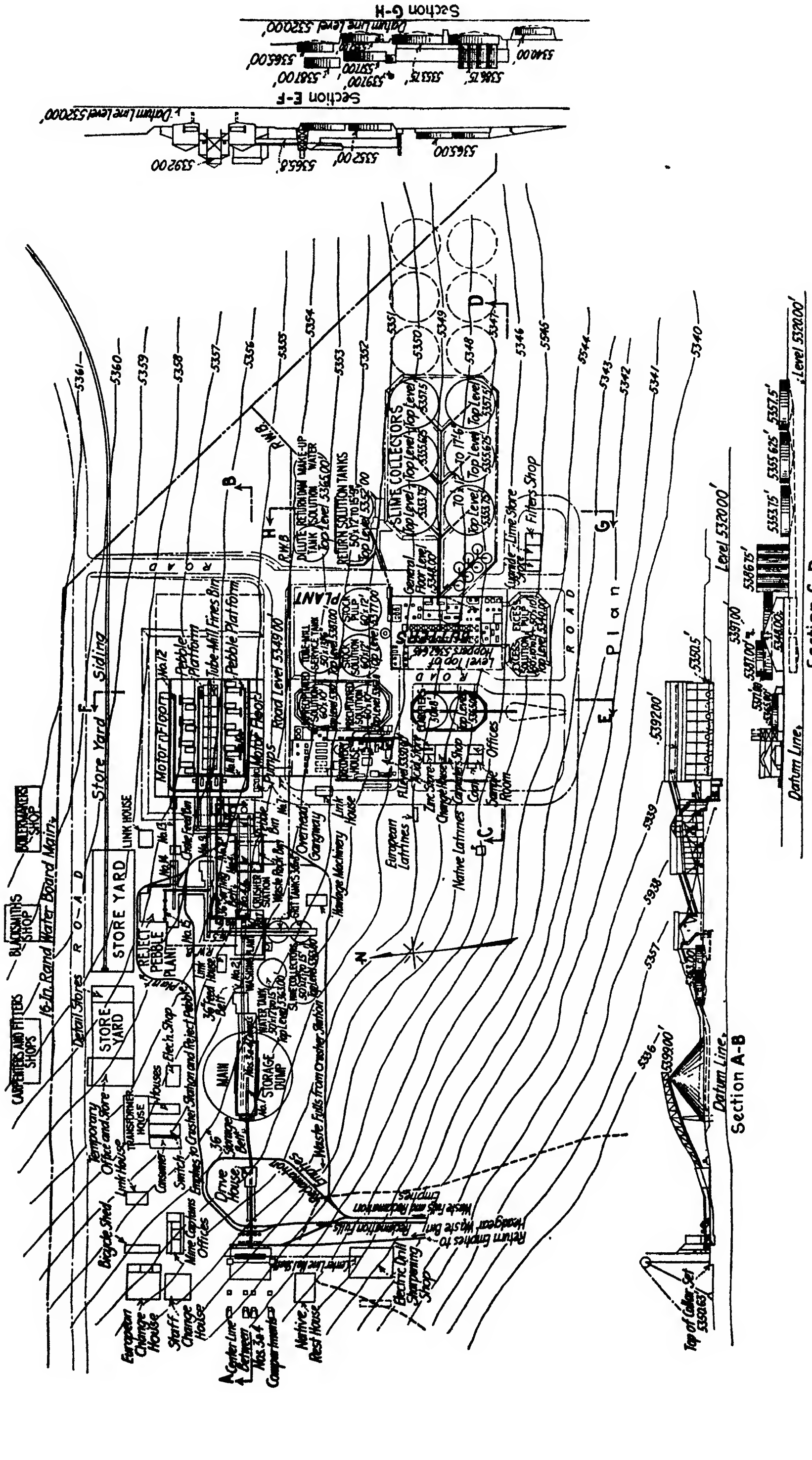


FIG. 6.—REDUCTION PLANT, WEST SPRINGS, LTD.

grading will be a very large tonnage producer. Although it is the practice on the Witwatersrand to discuss relative tube-mill performance in terms of −90-mesh product, the −200-mesh content of such product has a vital bearing on the extraction of gold contents. The existing Butters filter plants set a definite upper limit to the amount of +90-mesh permissible; at the same time, within such limit, considerable investigation is necessary to ascertain to what extent the Dorr classifier acts as a

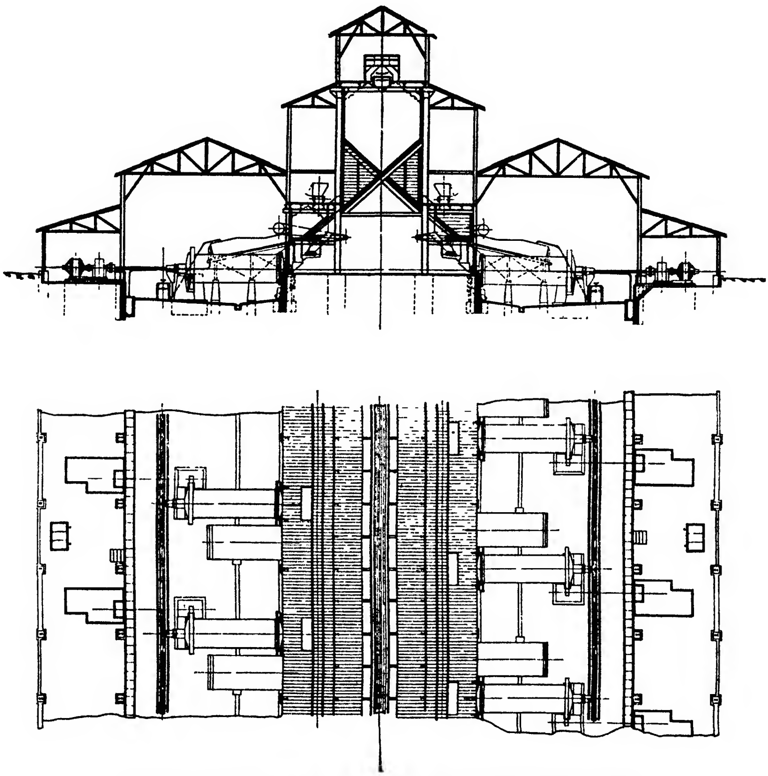


FIG. 7.—REDUCTION PLANT, WEST SPRINGS, LTD.

concentrator. In other words, whether the 2½ per cent. of +90-mesh mechanically permissible is economically justified.

The successful results obtained from the new section of the Springs Mines reduction plant resulted in the adoption of the same type of plant for West Springs, Ltd., this property being under the control of the same group, which reached the producing stage during April, 1924. In some ways, the full benefits of compactness of plant and consequent reduction in labor cost, increased ease of supervision, etc. could not be obtained at Springs Mines in as much as a large plant was already in commission and

the new plant had to be adapted to meet the existing topographical conditions and layout of the existing plant and property. At West Springs, however, a clear field was available; Figs. 6 and 7 give generalized elevations and cross-sections of the plant.

Starting from the headgear end of the plant, the stock pile, fed by a 36-in. conveyor on the steel cantilever, is a new feature in Rand practice. The usual type of headgear storage bin in these fields has a capacity of less than 1000 tons, which is more than doubled in the present case. It has been proved that this stock pile, by forming a large buffer between the more or less intermittent supply of ore from the mine and the reduction plant, which is continuously operated with the exception of Sundays, will greatly assist in maintaining the maximum output.

The washing plant is also somewhat unusual. The entering ore is thoroughly washed on a bar grizzly with ½-in. apertures. The washings from this grizzly are separated into three products—coarse gravel, sand, and slime. The coarse gravel, being thoroughly cleaned from adhering fines, joins the main stream to the tube-mill storage bins; the sands, having been leached in dewatering tanks, also join the main stream; and the collected slime is pumped directly to the main slime collectors. The object of this procedure is to obtain the maximum life of conveyor belts. Run-of-mine ore in these fields contains an unusually high percentage of fines and, as a result of the extremely liberal use of water in underground faces, is a most destructive material from the point of view of belt maintenance; in any case, it is necessary to wash the coarse material prior to sorting.

The sorting and crushing station is in such close proximity to the milling plant that supervision of the whole process of sorting, crushing, milling, and classification is greatly facilitated. As no amalgamation or blanketing process is practiced and as the ore is crushed in cyanide solution, the whole gold-recovery plant is compact and is housed in one building closely adjacent to the mill. In fact the layout is such that the chief reduction official, whose offices overlook the gold-recovery floor, can pass directly through the milling plant into the crushing and sorting plant under cover and on one floor level.

The tube-mills installed at West Springs are about 30 per cent. larger than the standard mills, being somewhat shorter but larger in diameter; the dimensions are 20 ft. by 6 ft. 6 in. For test purposes, a mill of this size was erected and run as an integral part of the Springs Mines plant for some time, with the following results:

Approximately 11,000 tons of ore was milled by this unit, the finished product being collected in a separate collector for measurement purposes. The average output per 24 hr. over the whole series of tests was 194 tons and the maximum 208 tons, the output, of course, varying in accordance with the grading of the product. Bearing in mind that the average

feed, including the crushed returned reject pebbles at West Springs, is likely to be considerably better than at Springs Mines and that grinding in cyanide is likely to permit of a slightly higher grading of product, with correspondingly increased output of the tube-mill, it was concluded that eight of these units would provide ample capacity for the monthly (26 days) output of 40,000 tons required at West Springs.

Up to the present, all the experimental work has been carried out with tube-mill liners of the Osborne bar type. This type has emerged, after many years of experience, as an effective and economical liner for a tube-mill handling stamp-mill pulp. It remains to be seen whether liners of a radically different type may not come into use for tube-mills handling a coarse dry feed. One or two new types are already in service at neighboring mines, and apparently give promising results as tonnage producers. Of course a mere increase of tonnage regardless of grading is easily obtained with the older type, but there is no doubt that the new process has opened a new field for liner experimentation.

By far the larger number of mills on the Rand are driven by a single-reduction countershaft belt-driven from the motor; in the Springs Mines and West Springs practice, a single-reduction enclosed gear with forced lubrication has replaced the belt drive. A considerable economy in power, floor space, and maintenance has resulted from this change.

Capital Expenditure

Appended is the original estimate of the capital cost of the plant to deal with 40,000 tons per month (of 26 days), together with certain basic rates on which the estimate was framed; the completion of the plant shows that this estimate has been closely adhered to. At a capacity of 40,000 tons per month, the cost of the plant is £6.17 per ton milled per month. The plant having been designed in all respects for ease of extension, any improvement in the daily tonnage of the existing tube-mills, up to an additional 10,000 tons per month, could be handled by the remainder of the plant without additional capital cost. It remains to be seen whether the new type of liner referred to will increase the capacity of the plant and, if so, to what extent. Should the existing eight tube-mills, some time later, reach a capacity of 50,000 tons per month, the capital cost of the plant per ton milled per month would then be a little under £5. When the condition of the mine warrants this increased tonnage, the authors will have attained a figure of capital cost which is better than that pertaining to the best of the large milling plants built on the Rand prior to the War, with the added advantage of considerably reduced running costs and, as far as the deep levels of the Far East Rand basin are concerned, an improved extraction amounting to the difference between 93.25 and 95.50 per cent.

For the sake of comparison, a careful analysis has been made of the capital cost of the Brakpan Mines plant, erected by the same parent group in 1909–1910 which, at the date of its going into service, was regarded as approaching the best in current practice. It has been necessary to re-price all the major items on the scale existing today; the result shows that today's cost of this plant would be £8.34 per ton milled per month.

In so far as the ordinary metallurgical results still arrived at by existing plants are concerned, it is difficult to see where the original Brakpan design should be seriously modified.

At present, the following monthly tonnages are being milled by this process:

	Tons	Tons
Springs Mines	35,000	
West Springs	40,000	
New State Areas	65,000	140,000

Extensions are being carried out at

Brakpan Mines	12,000	
West Springs	10,000	22,000

In addition to the above, an extension to one of the central Rand plants is contemplated having a capacity of	30,000
A new plant on the Far East Rand is now being designed to handle	50,000
So that in the near future the total monthly tonnage being milled on these fields by this process will be approximately	242,000

The tonnage crushed and treated at West Springs during the 25 working days of the month of June, 1924, was 35,740 tons. The power costs for the month at the rate of 0.525 pence per unit, were as follows:

	£.	s.	d.
Sorting and crushing, including washing plant and all main conveyor belts	73	15	0
Tube milling	1,651	2	6
Pulp elevating and classification	141	0	0
Reject pebble handling and crushing	14	0	0
Cyaniding slime	73	8	0
Air agitation	56	16	0
Butters filter plant	165	10	0
Precipitation and recovery	56	16	0
Return solution pumps	35	4	0
	£2,267	11	6

Thus the cost of power per ton crushed and treated is 15.22 pence.

ESTIMATED CAPITAL COST OF PLANT FOR 40,000 TONS PER MONTH AT WEST SPRINGS, LTD. REDUCTION PLANT

	£	£
Ore transport plant	.....	9,494
Transport by belt conveyors	9,494	
Sorting and crushing station		25,600
Buildings	4,180	
Washing and screening plant	8,450	
Sorting plant	6,100	
Crushing plant	6,870	
Tube-milling plant		66,600
Buildings	11,660	
Tube-milling equipment	41,720	
Pebble-handling plant	11,690	
Waste-removal plant	120	
Other equipment	1,410	
Pulp-elevating and classification plant		14,900
Buildings	500	
Pulp-elevating plant	1,200	
Classification plant	11,420	
Piping, launders, trestles and platforms	1,780	
Slime plant		92,900
Buildings	1,890	
Tanks and equipment	32,270	
Filter plant	41,460	
Compressed-air plant	1,470	
Pumps	4,540	
Motors and electrical equipment	3,770	
Piping, launders, trestles, and platforms	7,340	
Other equipment	160	
Waste-rock and residue disposal plant		3,800
Waste-rock disposal	1,910	
Slime disposal	1,060	
Slime dam	340	
Piping, launders, trestles, and platforms	490	
General water and solution services		5,800
Buildings	40	
Equipment	5,760	
Recovery plant		18,800
Buildings	3,740	
Precipitation plant	8,590	
Smelting and clean-up plant	4,280	
Motors and electrical equipment	1,220	
Piping, launders, trestles and platforms	920	
Other equipment	50	
Electric power and light supply plant		9,040
Main transformer station	4,600	
Subsidiary transformer and distribution stations	1,440	
Transmission and distribution plant	3,000	
Total		246,934

Cost per ton milled per month, £6.17

NOTE.—In the event of the mine reaching a condition that warrants a monthly tonnage of 50,000, it is possible, as already mentioned, that this could be milled with the existing plant, in which case the capital cost per ton milled per month would be reduced to £4.94. Should such expectations not be fulfilled, the alternative would be the addition of two tube-mills to the milling plant at a cost of £15,000. This would give a figure of £5.24 per ton milled per month.

Costs are based on the following data:

Excavations	1/9d. per cu. yd.
Concrete in place	42/– per cu. yd.
Steel tanks (second hand)	£18.13.6. per ton erected
Steel structural work (new)	£31.0.0. per ton erected
Timber	5/7d. per cubic foot
Average rate of European wages	24/– per day
Average rate of native wages	2/– per day

Operating Results at West Springs Mill[3]

The plant was started up in April, 1924, and went into full commission the following month without any difficulties being encountered. After a few months' operation, it was evident that the eight tube-mills installed were capable of handling 40,000 tons per month; as a matter of fact, in December the plant milled 41,050 tons. In view, however, of possibilities in respect of tonnage production, two additional tube-mills were installed, the first of which went into operation on Jan. 5 and the second on Jan. 19 of this year, thus bringing the nominal capacity of the reduction plant up to 50,000 tons. When this figure is reached, a corresponding improvement in the costs, as given here, may be anticipated.

Costs

In January of this year a new system of statistical records was introduced in the mines controlled by the Anglo-American Corpn. of South Africa, Ltd.; as this system makes many details of working costs more readily accessible, the period covered by January, February, and March of this year has been dealt with for the purpose of this paper. For this period, the general operations were as follows:

Tons hoisted from the mine	157,589
Tons from development dump	10,105
Total tonnage sent to sorting and crushing station	167,694
Eliminated by sorting, tons	32,304
Tons milled	134,400
Tons treated	135,861
Average reduction cost per ton milled over period	3/6.480d.

[3] On May 13, 1925, Messrs. Davis, Willey, and Ewing presented to the South African Institute of Engineers a paper embodying statements of tonnage treated with costs at the West Springs, Ltd. mill, for January, February, and March, 1925. This information is added to the original paper through the courtesy of the author and the South African Institute of Engineers.

This total reduction cost is made up under the following main heads, each figure being the average for the period:

	Pence
Sorting and crushing	7.0481
Tube-milling	20.6535
Cyaniding slime	8.4518
Butters filter plant	3.3320
Recovery	
Precipitation	1.9571
Smelting and osmiridium recovery	1.0375
Total	42.4800

Sorting and Crushing.—This section begins with the transport of ore from the headgear bins, includes the elevation of rock to and withdrawal from the stock pile, and ends with the delivery of the ore into the main tube-mill bins, embracing also the delivery of ore from the development rock dump, the disposal of all waste rock and the operation of the washing plant. The detailed costs of this section are as follows:

	Cost per Ton Milled, Pence	Cost per Ton Handled, Pence		Cost per Ton Milled, Pence	Cost per Ton Handled, Pence
White wages	0.4911	0.3946	Sundries and phthisis charges	0.1500	0.1205
Native wages	2.1071	1.6931	Workshops	0.4821	0.3874
Crusher spares	0.6661	0.5352	Power	0.3714	0.2984
Conveyer belt suspense account	0.5357	0.4305	Dump account	0.7982	0.6414
Oil and grease	0.1446	0.1162	Washing plant	1.3018	1.0460
			Total	7.0481	5.6633

Tube-milling.—This section begins where the previous section ends, and includes the milling and classification of tube-mill pulp and delivery of same to the main pulp-elevating pumps; also transport, sorting and crushing of reject pebbles. The detailed costs of this section are as follows:

	Cost per Ton Milled, Pence		Cost per Ton Milled, Pence
White wages	1.0464	Workshops	1.3696
Native wages	0.9250	Electric power	10.1821
Liners suspense account	1.0714	Air power	0.2983
Tube-mill spares, castings, etc.	1.7928	Assaying	0.1429
Conveyor belts	0.2179	Return solution service	0.1321
Sundry stores	0.1357	Dorr classification and tube-mill circuit pulp elevation	0.8750
Oil and grease, etc	0.3536	Reject pebble transport, sorting and crushing	1.4500
Lime	0.2286		
Electric material	0.0571		
Sundries	0.3750		
		Total	20.6535

Cyaniding Slime.—This process begins with the main pulp pumps, and includes slime collection, decantation, hosing, transfer to Pachuca agitating tanks and main pumps to stock pulp tank, also disposal of tailings and maintenance of slime dams. The detailed costs of this section are as follows:

	Cost per Ton Milled, Pence	Cost per Ton Treated, Pence		Cost per Ton Milled, Pence	Cost per Ton Treated, Pence
White wages	0.8196	0.8108	Workshops	0.1232	0.1219
Native wages	0.3929	0.3886	Electric power	0.3305	0.3269
Cyanide	2.9375	2.9059	Return solution service	0.1321	0.1307
Chemicals and assaying	0.0321	0.0318	Main pulp pumps	0.3929	0.3886
Lime	0.5769	0.5707	Air agitation	0.2071	0.2049
Lead acetate	0.2392	0.2367	Rand Water Board charges	1.7375	1.7188
Pump spares, etc.	0.3071	0.3038			
Sundries	0.2232	0.2208	Total	8.4518	8.3609

Butters Filter Plant.—This section begins at the delivery into the stock pulp tank and ends with the tailings discharge pumps. The detailed costs of this section are as follows:

	Cost per Ton Milled, Pence	Cost per Ton Treated, Pence		Cost per Ton Milled, Pence	Cost per Ton Treated, Pence
White wages	0.8696	0.8602	Sundries	0.2429	0.2402
Native wages	0.3661	0.3621	Workshops	0.1571	0.1555
Chemicals and acids	0.2393	0.2368	Electric power	0.9821	0.9716
Pump spares and castings	0.1964	0.1943	Air agitation	0.0696	0.0689
Oil and grease	0.0696	0.0689	Assaying	0.1393	0.1378
			Total	3.3320	3.2963

Precipitation.—This section begins at the solution clarifying tanks, embraces the Crowe-Merrill zinc-dust precipitation and ends with the barren solution pumps. The detailed costs of this section are as follows:

	Cost per Ton Milled, Pence	Cost per Ton of Solution Precipitated, Pence		Cost per Ton Milled, Pence	Cost per Ton of Solution Precipitated, Pence
Tons of solution precipitated = 244,418			Sundries	0.1268	0.0697
White wages	0.4196	0.2308	Workshops	0.0750	0.0412
Native wages	0.0660	0.0363	Electric power	0.2232	0.1227
Zinc dust	0.4964	0.2730	Assaying	0.0590	0.0324
Filter cloth and paper	0.2250	0.1237			
Chemicals and lead acetate	0.2661	0.1463	Total	1.9571	1.0761

Smelting and Osmiridium Recovery.—This section begins with the handling of gold zinc slime from Merrill presses, covers all other operations up to depositing the gold with the refinery authorities, and includes recovery of osmiridium. The detailed costs of this section are as follows:

	Cost per Ton Milled, Pence	Cost per per Fine Ounce Smelted, Pence		Cost per Ton Milled, Pence	Cost per per Fine Ounce Smelted, Pence
White wages	0.2500	0.6440	Sundries	0.1339	0.3450
Native wages	0.0286	0.0736	Workshops	0.0429	0.1104
Sulfuric acid	0.1375	0.3542	Assaying and electric power	0.0232	0.0598
Pots and liners	0.2054	0.5290			
Chemicals	0.1160	0.2990			
Coal	0.1000	0.2576	Total	1.0375	2.6726

Subaccount.—The eight subaccounts necessary for the building up of these costs are also reproduced in order to make the cost details as complete as possible.

Washing Plant

Tons milled	134,400
Cost per ton milled	1.3018d.

	Cost per Ton Milled, Pence		Cost per Ton Milled, Pence
White wages	0.1375	Workshops	0.2588
Native wages	0.3696	Electric power	0.0465
Conveyor spares, castings, etc	0.2036	Rand Water Board—water	0.1250
Lime	0.0679		
Sundries	0.0929	Total	1.3018

Main Haulage Dump

Tons waste sorted	32,304
Tons reclaimed	10,105
Tons waste from mine	6,650
Total tons handled	49,059
Cost per ton handled	3.1945d.

	Cost per Ton Handled, Pence		Cost per Ton Handled, Pence
White wages	0.3229	Workshops	0.2250
Native wages	2.1526	Power	0.1565
Oil and grease	0.1076		
Sundries	0.2299	Total	3.1945

Reject Pebbles

Tons transported	33,677
Tons sorted	2,136
Tons crushed by disk crushers	31,541
Tons milled	134,400

	Cost per Ton Milled, Pence	Cost per Ton Crushed by Disk Crushers, Pence		Cost per Ton Milled, Pence	Cost per Ton Crushed by Disk Crushers, Pence
White wages	0.0321	0.1369	Sundries	0.0411	0.1750
Native wages	0.5376	2.2904	Workshops	0.2071	0.8827
Crusher spares	0.4554	1.9403	Electric power	0.0946	0.4033
Conveyor spares	0.0821	0.3500			
			Total	1.4500	6.1786

DORR CLASSIFICATION AND TUBE-MILL CIRCUIT PULP ELEVATION

	Cost per Ton Milled, Pence
White wages	0.1964
Castings	0.0393
Sundries	0.0393
Workshops	0.0732
Electric power	0.5268
Total	0.8750

MAIN PULP PUMP

Cost per ton milled.................................. 0.3929d.

RETURN SOLUTION SERVICE

Cost per ton milled.................................. 0.2642d.

AIR AGITATION

Cost per ton milled.................................. 0.3482d.

ASSAYING

Cost per ton milled.................................. 0.1175d.

All these figures are taken from the mine accounts, which are framed in the form given. In connection with these costs, we would draw attention to one or two items of expenditure which are somewhat unusual:

Rand Water Board Water.—The cost of water charged to the plant is is 1.8625d. per ton milled; this is because the mine has extremely limited sources of water at its own disposal.

Compressed air for pulp agitation is supplied by a separate plant, which is a direct charge to reduction costs. Compressed air is also used for other services, such as air lifts for floor drainage. The amount of air so used is metered and debited at cost of production. In the same way, all repair work that is not carried out as a direct charge against the reduction plant, is debited at current workshops cost. Native labor is charged at the current mine rate.

Suspense Accounts.—Certain items of material, as tube-mill liners, conveyor belting, etc., are dealt with on a fixed basis per month; in other words, by means of Suspense Accounts. The amounts of these are calculated to meet safely the average annual expenditure of such items, and are considered to be on a very conservative basis.

Running Time.—During the period under review, the tube-mill plant ran for 97.135 per cent. of the possible running time (*i. e.*, 144 hr. per week). Ordinary stoppages accounted for 2.095 per cent. of the time lost, and the remaining 0.770 per cent. is accounted for by failure of the main power supply.

Running Staff.—The number of white men employed in the reduction plant is twenty-five, which includes three sectional managers, one clerk, one grader, and four mechanics.

Power Consumption.—During the period under review, the consumption of electricity amounted to 27.04 kw.-hr. per ton milled, corresponding to a cost of 12.308d. per ton milled. The consumption of the electrically driven air compressors for slime agitation is, of course, included in the foregoing. Power for tube-milling alone amounted to 2,708,019 kw.-hr. The grading of the final product was

60	+90	+200	−200
Nil	3.30%	23.37%	73.33%

so that 96.7 per cent. of 134,400 tons of −90 mesh was produced for this figure, or 20.83 kw.-hr. per ton of −90 mesh produced.

General Notes on Operation

Perhaps the most essential feature of the West Springs plant is that it was designed with the intention of grinding all the ore much finer than is ordinary Rand practice, particularly on the Central Rand where, from the nature of the ore and type of existing plants, such fine grinding is not economically desirable. It is, of course, possible to grind to almost any degree of fineness by stamp milling only; and, with a greater degree of economy, by stamp-milling *cum* tube-milling. The production of a pulp of approximately the same degree of fineness as that for which the West Springs plant is designed has been attained in one or two plants of standard type, but the conditions have been abnormal, inasmuch as the capacity of the reduction plants have been, owing to extraneous causes, considerably in excess of the monthly tonnages available for milling. The authors' experience in this connection may be summarized as follows:

In December, 1923, and January, 1924, a two months' test was carried out on the original stamp-mill-tube-mill plant at Springs Mines, Ltd. This test consisted in producing a pulp of the same average grading as that being produced in the new so-called "all sliming" section of the plant. Throughout these two months, a product of similar grading, resulting in a similar residue value, was produced in the two sections. At the end of the period a careful comparison of the costs on the original plant when producing this finer product, with the costs during the preceding four months, when the normal grading of

+60	+90	−90
0.5 to 1%	8 to 10%	90 to 92%

was being produced, showed an increase in the cost of stamp-milling and tube-milling of 6.061d. per ton milled.

The costs now put forward will probably compare favorably with those pertaining to the older type of plant in spite of the considerably increased fineness of grinding and the capital cost involved is considerably less.

Sorting and Crushing Plant

As the milling process is carried out in cyanide solution, it was decided that a thorough preliminary alkaline wash would be desirable, so the washing process was made as complete as possible in order to minimize wear of conveyor belts.

A year's experience of conveyor maintenance has more than confirmed the view that good washing is essential to a good belt life. In the washing process during this period, 1340 tons of slime, with a grading analysis of $\frac{+200}{20\%}\ \frac{-200}{98\%}$ was eliminated and pumped direct to the slime plant for treatment; this quantity is 1 per cent. of the total ore milled.

Belt Conveyors.—The automatic feeder employed on the 36-in. belt feeding run-of-mine ore to the stock pile, and the 36-in. conveyor feeding the sorting and crushing plant, has given exceedingly good results, because of the careful design of the chute angles and the speed of delivery in relation to the belt speed. These belts have each carried 585,000 tons of run-of-mine ore and show so few signs of wear and tear that, barring accidents, their life should be about three years. Throughout the conveyor plant, as far as possible, incoming ore is cushioned on a bed of fines, which the mechanical feeders provide automatically. As the total feed to the tube-mill bins is practically all 1¾-in. material and has been thoroughly washed, an automatic tripper is used for feeding the tube-mill bins instead of the more common shuttle belt. No difficulties of any kind have attended the use of the tripper. There appears to be a considerable saving in labor cost, and a good mixture of the ore in the bins is easily secured. The latter is an important point in a plant of this nature.

The sorting and crushing plant is fed by a single automatic feeder by which the hourly rate of flow of run-of-mine ore into the plant can be closely regulated. A steady flow of ore is an important factor in the general capacity and efficiency of a sorting and crushing plant. A complete warning-bell system, with push buttons at all strategic points, together with a push-button control system operating on the no-voltage release of the driving motors, enables the main feeder, or any belt, to be stopped instantaneously from a number of points in case of accident, choking of chutes or other eventualities. This arrangement has many times prevented damage to belts and gears, and has saved its initial cost several times over.

Crushing.—Crushing is carried out by two gyratory crushers of standard type, fed from steady-head bins containing about an hour's supply of ore per crusher. This enables a continuous choke feed to be main-

tained, which greatly improves the product from the crushers, and the steady-head bins minimize the effect of temporary stoppages in the flow of ore through the plant. The sorted waste bins are large, and the bottom is formed of waste rock inside the angle of repose resting on the solid ground. The sorting-belt floor is hung from the roof principals instead of being supported by posts going down through the waste bins. This design is not novel, but is excellent in that it reduce the maintenance of bin linings to a minimum.

Tube-milling Plant.—The back-to-back arrangement of plant lends itself to easy and, therefore, good supervision; furthermore, ample space and good daylight are required in a lay-out of tube-mills and Dorr classifiers. The ordinary double-sided bin commonly used in back-to-back stamp-mill practice, does not permit of these conditions being satisfactorily attained. The type of bin actually adopted insures ample light at the head, or feed, end of the tube-mills, and permits the tubes on opposite sides of the building to be staggered on 30-ft. centers, thus giving ample space and daylight, at the same time allowing the bins to be self-emptying. The ordinary type of belt drive for tube-mills has been replaced by enclosed single-reduction gears, the gearboxes being fitted with "Michell" bearings and automatic lubrication throughout. The wear and tear of these gears is inappreciable after 12 months' service, and points to a long life. They have reduced maintenance cost greatly and considerably increased mechanical efficiency. With the adoption of these gears, all difficulties in starting tube-mils, that have been standing for some hours, have disappeared. In a plant that is shut down for 24 hr. every week, the aggregate loss of time in starting-up tube-mills is appreciable.

In a closed tube-mill-Dorr-classifier circuit, it is necessary to introduce some device for elevating pulp from the tube-mill outlet to the classifier, or the classifier oversize to the tube-mill. The ordinary scoop method for elevating the latter product into the tube-mill was found impracticable because of the size of the tube-mill and classifier units used. Recourse was, therefore, had to supplying the necessary solution, required for classification, under pressure to a hydraulic jet, and thereby elevating the tube-mill effluent to the classifiers. This method is by no means perfect. The mechanical efficiency of the process is probably not more than 8 per cent., as refinements in the form of jet to attain better efficiency mainly result in increased maintenance costs. On the other hand, the device is extremely simple and effective in operation, and automatically maintains the correct ratio of dilution, which is very necessary for consistent classification.

The Dorr classifiers, which are 8 ft. wide and 18 ft. 4 in. long, are operated at thirteen strokes per minute. The average grading of the finished product of the overflow of the classifier is

+60	+90	+200	−200
Nil	3.30%	23.37%	73.33%

and the average grading of the oversize return to the tube-mill

+60	+90	+200	−200
39.2%	33.3%	21.1%	6.4%

the ratio of dilution in the classifier overflow being seven of solution to one of solids.

The quantity of selected grinding pebble added to the tube-mills averages 27 tons per tube-mill per 24 hr. This quantity is about 7 tons higher than was anticipated from the result of experimental work on the same size of tube-mill carried out at Springs Mines, Ltd. The difference is attributable to a lack of sufficient pebbles of really suitable shape and size, which deficiency must be made up by the addition of pebbles of a slabby and, therefore, more easily fractured form.

While the experimental work carried out with certain types of tube-mill liners was by no means final and conclusive, results obtained seemed to show that, within the very narrow limits of grading imposed by the necessity of obtaining a specified residue from the ore treated, no particular advantage pertained to these liners over that obtainable with the ordinary Osborn bar type. It must be borne in mind, however, that with a wider range of grading, results might have been quite different. A point worth mentioning is that the increased diameter of the tube-mills does somewhat increase the difficulty of securely wedging the ordinary Osborn bar lining. A modification of the ordinary procedure quite overcomes this difficulty; it consists mainly in a special locking ring in the middle of the length of the tube-mill.

The reject pebble to be handled in this plant is considerably more than that handled in ordinary practice; the total figure, for the period under review, is 33,677 tons. The handling of these pebbles is entirely automatic; they are delivered by belt to the reject-pebble sorting and crushing plant. The reject material is composed of approximately 50 per cent. reef and 50 per cent. waste. The sorting of pebbles from 1 in. to 1½ in. diameter is, of course, an expensive process per ton sorted, which is reflected in the cost of native labor given above under this head, but every ton eliminated at this point bears no further cost of cracking, tube-milling and treatment; also it makes room for a ton of new ore of the average grade of ore milled. The pebbles are cracked in disk crushers, the object being not so much to obtain a fine product as to obtain fresh angles for attrition in the tube mill. It is, of course, very important to keep tramp iron out of crushers of this type; this has been attained by a simple magnetic device.

The average grading of this material after cracking is as follows:

+1 in.	+½ in.	+¼ in.	+60 mesh	+90 mesh	+200 mesh	−200 mesh
Nil	6.2%	28.1%	60.1%	1.9%	1.2%	2.5%

Cyaniding Slime.—The finished product from the tube-mill plant is elevated to six slime collectors 70 ft. in diameter by 12 ft. high, with 5 ft. 6 in. coned bottoms. The solution overflows into internal peripheral launders and gravitates to storage tanks for return to the tube-mill circuit, a sufficient quantity being withdrawn daily and sent to the precipitation plant to maintain the mill circuit at a figure of approximately 2.5 dwt. per ton of solution. In order to minimize the amount of pumping required for decantation of the remaining solution in the collectors, the tanks are interconnected by 8-in. pipes placed about halfway up the sides. The settled slime is transferred to Pachuca air agitating tanks in the usual way, except that separate pipelines are provided for filling and emptying these tanks. This is done to reduce the amount of contamination of treated pulp to a minimum. This arrangement also shortens the cycle time of operation. The grading of the final product from the tube-mill plant being somewhat coarser than that usually dealt with in ordinary slime and Butters filter plants, the grade of all piping carrying the final product is correspondingly increased. The average time of agitation is 12 hours.

Butters Filter Plant.—This plant consists of sixteen hoppers containing 448 leaves; the average time taken per complete cycle is under 100 min., made up as follows:

	Minutes
Filling	8
Taking on cake	12 to 15
Emptying excess pulp	6
Filling with solution	6
Washing	35
Sampling and dropping cakes	10
Emptying excess solution	10
Discharging to residue pit	5

The thickness of cake varies from 1½ to 1⅝ in. The time required for hosing out the residue pit and pumping to the dam varies from 45 to 60 min. The average charge treated per cycle is 220 tons.

Recovery.—Precipitation is carried out by the Crowe-Merrill zinc-dust process in three 40-frame, 54-in. filter presses. The average quantity of solution precipitated is 64 tons per press per hour, two presses being normally in operation. Presses are cleaned up twice per month and, after acid treatment and calcination, the gold slime is smelted in a reverberatory pot furnace. The slime after acid treatment averages 35 per cent. gold, and after calcination 60 per cent.

Owing to the extreme difficulty in prognosticating the extent and values of the occurrence of metals of the platinum group on these fields, it was not considered advisable to install an elaborate plant for the sole purpose of increasing the recovery of these metals. This view was strengthened by experimental work at Springs Mines in the latter part of

1923, which showed that an appreciable amount of osmiridium was locked up in the tube-mills, and this could be recovered by a simple process of treatment of the tube-mill concentrates. In 1924, at Springs Mines, Ltd., this method yielded 260 oz. of osmiridium concentrates from a total of 770,000 tons milled, at a quite inappreciable cost of recovery, and during the three months under review West Springs actually recovered 17.5 oz. from current milling operations.

General.—The following figures of working results obtained in the treatment plant for the period under review may be of interest:

Tons treated	135,861			
Average residue grading	+60	+90	+200	−200
	Nil	3.50	21.97	74.53
Average value of residue	0.464 dwt.			
Average value of undissolved gold in residue	0.422 dwt.			

Consumption of Stores

Cyanide	0.309 lb. 100 per cent. NaCn per ton treated
Zinc	0.076 lb. per ton treated
Lime	2.458 lb. per ton treated
Sulfuric acid	0.072 lb. per ton treated
Hydrochloric acid	0.093 lb. per ton treated
Lead acetate	0.038 lb. per ton treated

The grading results given throughout, with the exception of those for the disk crusher product, are obtained from the use of Locker's standard screens of the following dimensions:

Apertures per Linear Inch	Diameter of Apertures, Inch	Diameter of Wire, Inch
60	0.010	0.0048
90	0.006	0.0036
200	0.003	0.0020

Since these notes were compiled, the results for the month of April have been received; these show that the tonnage milled was at the rate of 50,000 tons for a 27-day working month, and that the total reduction costs amounted to 3s. 3.627d. per ton as compared with the figure of 3s. 6.480d. for the period covered by this paper.

In conclusion, the authors' thanks are due to the Chairman and Directors of the Board of West Springs, Ltd., for their permission to put forward the figures and results contained in the foregoing notes.

DISCUSSION

Charles E. Locke, Cambridge, Mass.—In this country, we have come to think that we should use smaller size of feed in our ball-mills.

I will admit that a ball-mill is not comparable to a tube-mill, as conditions may not be the same, but there we have an unusual demonstration of the advantage of a coarser feed. Further investigation along this line is going to lead to some valuable results. The authors have overcome the difficulty of this coarse feed by taking out what I would call the difficult lumps. It is not clear from the paper whether many of these difficult lumps may not be reduced portions of their grinding media.

H. W. Hardinge, New York, N. Y.—The idea is not exactly new because in 1911 they used the miner to reduce the finer material. We proceeded three or four years using many tons, about 15 tons or nearly the same proportion of ore to grinding medium. Another thing to be taken into account is the hardness of the ore being ground. In South Africa, the transportation costs must be taken into account. They are also making progress in the method of using tube-mills and ball-mills instead of stamps. Experiments are to be conducted with 10-ft. diameter mills there, with the object of increasing the mass action and agitation which, as has been demonstrated under different circumstances, increases the overall efficiency.

In 1902 or 1903, I operated tube-mills of 20 ft. in length. My next mill was reduced to 8 ft. in length, my next was 6 ft. in length. We got the same results. I think the length of a tube-mill is a question that might be carefully looked into. I do not like to say much about it, because it takes more or less of a commercial rather than a technical aspect but I have only given the facts as I have observed them.

H. N. Spicer, New York, N. Y.—Since the paper was written, the authors have been following up that line of work and I have received the results of several months' experiments on running a Dorr bowl classifier, instead of the straight classifier in closed circuit with a tube-mill. I have not had time to analyze these closely but they show that on a percentage basis the relative efficiencies work out as follows: Cone, 100; straight Dorr classifier, 117; Dorr bowl classifier, 125. The authors are apparently satisfied that the extra benefits to be derived from the use of the bowl machine warrant its introduction, as it leads to an increased tonnage per grinding unit. The production of +90-mesh material is reduced and the smaller amount of undersize returning to the mill is a marked benefit.

G. M. Brown, New York, N. Y.—While connected with a company operating in northern Canada, I had an opportunity to observe results obtained from tube-mills of different lengths. The first tube-mill installed was 5 ft. in diameter by 22 ft. long and was operated in closed circuit with a Dorr Model C duplex classifier. Later, an additional unit was needed so a tube-mill 5 ft. in diameter and 16 ft. long was

installed and operated in closed circuit with a Dorr Model C duplex classifier. Each of the tube-mills handled the oversize product from a 6 ft. by 22 in. Hardinge ball-mill. Each unit handled 150 tons of ore and the screen analysis of each classifier overflow averaged about 85 per cent. −200-mesh. While the 16-ft. tube-mill required less power and appeared to do about the same amount of work as the 22-ft. mill, it was noticeable that the classifier in closed circuit with the shorter mill carried a heavier circulating load and the mill had a greater tendency to overload.

H. W. Hardinge.—The Anaconda Copper Mining Co. originally used mills 10 ft. in diameter. They reduced them to 7 ft. in diameter, but after about 6 years increased the diameter to 10 ft. and obtained considerably greater efficiency. The present capacity is fully 20 per cent. greater for the same power than was obtained with the long mill of smaller diameter.

G. M. Brown.—I am informed that the Anaconda Copper Co. wished to handle a large circulating load and reduce the moisture content of the returned sands. They, therefore, installed a 60-in. Akins classifier to operate in closed circuit with one of their Hardinge mills. I understand that at certain periods this classifier handled a circulating load of approximately 2000 tons per 24 hr., at the same time overflowing approximately 500 tons of finished −48-mesh material. However, the average operation was a circulating load of approximately 1500 tons with a classifier overflow of 400 tons of finished material.

Justice F. Grugan, New York, N. Y.—With regard to the pebbles, I was much impressed with the irregular character of these masses of silica. They are not like the ordinary round pebbles used in crushing. The Rand pebbles are about 4 to 4½ in. wide and from 8 to 12 in. long and irregular in shape. Just what effect in crushing that irregular size might have I do not know.

H. N. Spicer.—I have seen a tube-mill give out and have watched it being emptied. The pebbles as a whole become rounded.

R. C. Canby, Wallingford, Conn., (written discussion).—The feeding of coarse ore into the tube-mill, with the resulting increased capacity, recalls my experience at La Luz mill, of the Montezuma Lead Co. at Santa Barbara, Chihuahua, Mexico in 1902 or 1903. The 6-ft. "Monadnock" Chilean mills (Wellman-Seaver-Morgan Co.) had an apparent maximum capacity of about 30 tons upon the comparatively fine jig tailings. From my examination of the action of the material in the mills, I determined to try adding, with the jig tailings, some coarse ore, and was successful in adding as much again of ore passing a 2-in. ring. The annular feed troughs of the mills were replaced by annular troughs having the bottoms especially designed to allow the coarse ore to fall to

the vertical feed pipes, delivering the feed onto the ring die directly in front of the rollers. This coarse ore was fed dry directly into the annular mill feed troughs. By this means of adding to the 30 tons of tailings, with the conveying water, 30 additional tons of through 2-in. material, dry, the swash was reduced, and the pulp thickened. The coarse ore was a selected ore having but little galena sufficiently coarsely disseminated to have made any considerable proportion of jig concentrate. No coarse ore was removed from the mills, but the feed of coarse ore was suspended at times for brief periods if the mill showed overload. While this procedure did practically double the Chilean-mill capacity, it was not well adapted to Chilean-mill practice because of the greatly added screen wear, when using punched slotted screens. It convinced me quite fully as to the inadaptability of Chilean and Huntington mills for the work, to which they were so largely put in those days, and in the case of the Chilean mill, at least, the coarse ore performed much more of a function than providing easily breakable angles.

Determination of Dissolved Oxygen in Cyanide Solutions

By A. J. Weinig,* Met. E., and Max W. Bowen, Golden, Colo.

(New York Meeting, February, 1925)

The important part that dissolved oxygen plays in the cyanide treatment of gold and silver ores is commonly recognized by most metallurgists and mill men. But heretofore there has been no simple method on which the mill man could rely for determining the amount of oxygen in the various mill solutions. A few methods are adaptable to the laboratory, such as the gasometric[1] determination by actually measuring the oxygen, Winkler's[2] iodometric method, and Schutzenberger's[3] method, which depends on the reducing action of sodium hyposulfite on a blue solution of indigo carmine; but these are not readily adaptable to the needs of the mill man and cannot be applied to cyanide solutions without modification. The gasometric method is the most accurate but it takes too long to complete a determination. White's[4] method (a colorimetric method that depends on the degree of coloration imparted to a solution of pyrogallic acid in the presence of caustic soda) although much more rapid than any of the methods named, often gives misleading results on account of grading of colors of different solutions, which nearly always contain various kinds of salts.

The method herein described was devised for the use of the mill man, the aim being to develop a simple, practical, accurate method. It is a modification of the Schutzenberger method and depends on the reducing

* Director of Experimental Plant, Colorado School of Mines.

[1] Augustus H. Gill: Gas and Fuel Analysis for Engineers, 39. John Wiley & Son, New York. Hemple's Gas Analysis, Translation by Dennis.

C. Lunge and C. A. Kean: Technical Methods of Chemical Analysis, **1**, 5, 189. Van Nostrand, New York. Technical Gas Analysis, Winkler and Lunge, 68–100.

[2] *Jnl.* Soc. of Chem. Ind., London (1889) **8**, 727.

[3] *Jnl.* Soc. of Chem. Ind., London (1889) **8**, 729.

[4] *Jnl.* of Chem. & Met. & Min. Soc. of S. A. (1918).

Edward M. Hamilton: Manual of Cyanidation, McGraw Hill Book Co.

action of a sodium hydrosulfite solution on a solution of indigo blue indigotin-disulfonate. The method determines oxygen accurately to tenths of a milligram per liter of solution or one part of oxygen in 10,000,000 parts of solution on a 250 c.c. solution sample, with a proportionately greater degree of accuracy on larger amounts of solution samples.

Saturation of Oxygen in Solution

In this paper, the saturation of oxygen in solution is taken as that maximum quantity of oxygen which dissolves from free air,[5] which is very much less than the quantity of oxygen that dissolves in pure water from an atmosphere of pure oxygen.[6] The amount of oxygen that dissolves in water depends on the atmosphere from which it is derived and, except in the case of hydrogen,[7] this solubility is well explained by Dalton's law of partial pressures of gases.[8] Salts dissolved in the water also affect the oxygen solubility but, under the usual concentrations found in practice, this is relatively unimportant. The oxygen content of air-saturated water is a function of the pressure and temperature; Winkler's results are shown in Fig. 1. From this chart, the saturation point can be quickly determined for all localities and temperatures.

Altitude-pressure and Standard Saturation Curves

Chart *A*, Fig. 1, is used to determine barometric pressures at various altitudes; chart *B* is used to determine standard saturation values for various temperatures and pressures. In chart *A*, altitudes, in feet, are plotted on the horizontal axis and pressures, in millimeters, on the vertical axis. To find the pressure corresponding to a certain altitude, follow the elevation line downward to its intersection with the curve *X* then horizontally to the right and read the pressure. For example, if the elevation is 6000 ft., the 6000-ft. line is followed to its intersection *O* with the curve *X* then the corresponding pressure, 607 mm., is obtained from the right-hand side of the chart.

In chart *B*, temperatures are plotted on the horizontal axis and the amount of oxygen, in milligrams per liter of distilled water, is plotted on the vertical axis; various pressure curves also are plotted, as shown. To find the saturation value for a certain temperature and pressure follow the temperature line upwards until the point corresponding to a given pressure is reached, then follow horizontally across to the left-hand side of the chart and read off the amount, in milligrams, of oxygen per liter of

[5] Winkler: *Op. cit* (1901) **34**, 1440.
A Dictionary of Chemical Solubilities, Inorganic, 2.

[6] Winkler: *Op. cit.* **24**, 3609.
A Dictionary of Chemical Solubilities, Inorganic, 635.

[7] *Jnl.* Soc. of Chem. Ind., London (1889) **8**, 729.

[8] Reed and Guthe: College Physics, 118.
Peele: Mining Engineers' Handbook, 2052.

solution. For example, to determine the amount of oxygen in a solution having a temperature of 59° F., at an elevation of 6000 ft. It has already been found that at an elevation of 6000 ft. the pressure is 607 mm.; therefore the 607-mm. pressure curve must be used; that is, it is necessary to interpolate between the 600-mm. and the 650-mm. curves. The 59° F line is followed to its intersection *R* with the 607-mm. curve, then from the left-hand side of the chart is read off 8 mg. of oxygen per liter. The same procedure is used for the various pressures, using the curve corresponding to the particular pressure. For any particular plant, a solubility curve for that elevation should be plotted.

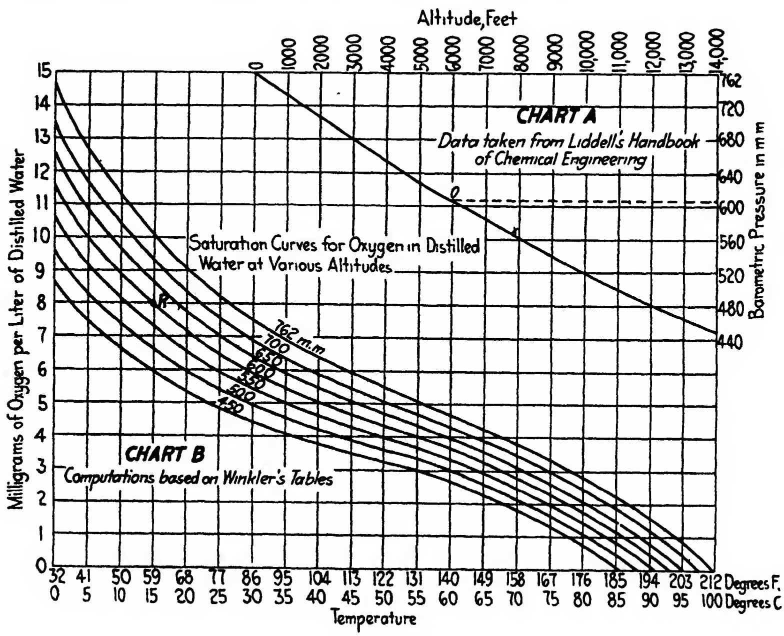


FIG. 1.

Oxygen-saturated Water or Solution

Our standard for comparison is air-saturated water or solution. This is best made by placing 1 liter of water or solution in a 2-liter Winchester bottle and violently blowing air through it. With distilled water or pure tap water, 20 to 30 min. aeration will insure saturation; but with mill solutions that contain hydrogen, saturation can only be attained by aerating at least for an hour. Solutions fresh from precipitation saturate with great difficulty; it may take several hours aeration to wash out the dissolved hydrogen before complete oxygen saturation can be attained. After this aeration is completed, the solution should remain for ½ hr. or longer at a constant temperature to insure the complete elimination of finely disseminated undissolved air bubbles, which would otherwise inter-

fere. When using water for this standardization, it is well to add a little lime before aeration so as to produce alkalinity similar to the conditions found with cyanide solutions. This alkalinity does not materially affect the solubility of oxygen but is desirable so that the following procedure may be as near like that of cyanide solution as possible. When convenient, it is desirable to use distilled water.

Apparatus

The apparatus required for this test are: Two Winchester acid bottles *a*, *b*, Fig. 2, 2½ liters capacity; one 250-c.c. flask *c*, one 50-c.c. burette

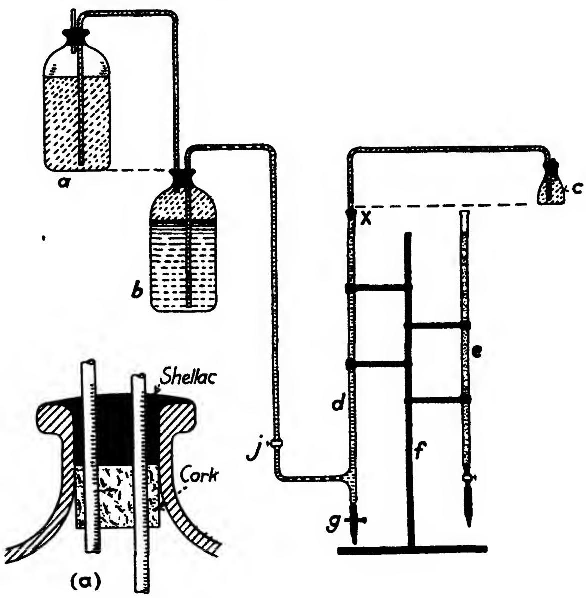


Fig. 2.

d with side connection; one common 50-c.c. burette *e*; one clamp stand *f* to hold burettes in position; one 400-c.c. beaker with the 250-c.c. point marked on it; one special glass stirring rod, shown in Fig. 3; glass or lead tubing (3⁄16 in.) for connections; rubber tubing for connections; one pinch cock *g* for bottom of rubber connection on burette that contains standard hydrosulfite solution; one container for kerosene to be used in the procedure.

When setting up the apparatus, the relative position of the different parts shown in Fig. 2 must be closely followed. As there is a siphoning action from bottle *a* to bottle *b* and from bottle *b* to the burette *d*, the bottom of bottle *a* must be above the top of bottle *b* and also above the top of the burette *d*; also the bottom of the flask *c* should be above top of the burette *d*, for convenience. Bottle *b* contains the standard solution;

as this standard deteriorates very rapidly, if exposed to the air, the bottle must be sealed air tight. This may be done in the following manner: Place a cork—not rubber—with two holes for the tubing in the neck of the bottle so that there is about 1 in. between the top of the cork and the top of the neck of the bottle, as shown in (*a*) Fig. 2. Place the tubing in the cork as shown, then pour melted shellac above the cork so as to fill the space completely. Care must be taken not to break the tubing or the neck of the bottle with the hot shellac; this danger may be avoided by having the glass perfectly dry and heating it before pouring in the hot shellac.

The bottles are filled in the following manner: Remove the connection *x* and place a cork in the top of the burette *d* so that no solution can overflow. Place a bottle containing 2½ liters of kerosene so that its bottom is above the top of bottle *a* and connect this bottle to the bottom of the burette *d* with a siphon. Open the pinch cock *g* and the stop-cock *j* and allow kerosene to siphon into bottle *b* until it is filled. Replace the bottle which contained kerosene by a bottle containing the standard solution of hydrosulfite. This solution should always be covered with a layer of kerosene; siphon the standard solution into bottle *b*, the kerosene being forced from bottle *b* over into bottle *a* automatically. As soon as the standard hydrosulfite solution has reached to within 1 or 2 in. of the top of bottle *b*, close both the pinch cock *g* and the stop-cock *j*. After the flask *c* has been nearly filled with kerosene, place the connection *x* in top of the burette *d* and seal with dry shellac dissolved in alcohol. Open the stop-cock *j*, the pinch cock *g* being kept closed, and allow the standard solution to pass into the burette *d* until it just enters the flask *c*; then close the stop-cock *j*, open the pinch cock *g*, and allow the standard solution to drain out completely; its action as a siphon will draw the kerosene over into the burette *d*. The standard solution is now drained off so as to eliminate any possibility of its being exposed to air and to give it a cover of kerosene in the burette *d*. Close the pinch cock *g*, open the stop-cock *j*, and allow the burette *d* to fill to the zero mark. The layer of kerosene prevents the admission of air during this procedure. Then the apparatus is ready for use. Fill the burette *e* with the indigo disulfonate solution and place a test tube or glass cover over the top to prevent evaporation.

Standard Solutions

A very convenient amount of standard sodium hydrosulfite solution is made up as follows. Fill a Winchester acid bottle, 2½ liters capacity, with distilled water. Preferably it should be freshly distilled so as to be as free from oxygen as possible but this is not essential. Dissolve 5 gm. of sodium hydroxide in this bottle by gently revolving. When all the sodium hydroxide is dissolved, add 5 gm. of sodium hydrosulfite to the

solution and immediately place a layer of kerosene over the solution. When all the salts are dissolved, siphon into the bottle *b* for standard solution. The caustic soda preserves the hydrosulfite and enters into the reaction during titration.

The indicator, indigotin disulfonate, is made up as follows: Place in a casserole 7 gm. of indigotin and add 30 c.c. of concentrated sulfuric acid. Place over water bath and heat to 90° C. for 1½ hr., or until all lumps disappear. Then dilute to 2 liters with distilled water. Neutralize the acidity by adding powdered limestone, small portions at a time, and allowing it to stand for a few minutes between additions, until all action has ceased. Filter without washing, place in a corked bottle, and use as necessary in the procedure. It is convenient to dilute this solution so that 1 c.c. of the indicator is equivalent to 0.25 mg. of oxygen per liter of solution. This will indicate 1 gm. per liter when a solution sample of 250 c.c. is taken for titration.

Chemistry of the Process

The process is based on the reducing action of sodium hydrosulfite on the indigo after all the oxygen in solution has been titrated and thereby changes the indigo blue to indigo white. As both the indigotin and hydrosulfite are impure products, as produced commercially, the exact chemical formula for them or the equation showing the above reaction cannot be given absolutely; however, the following shows the nature of the reactions.

Indigo blue = $C_{16}H_{10}N_2O_2$, as disulfonate = $C_{16}H_8N_2O_2(SO_3H)_2$
Indigo white = $C_{16}H_{12}N_2O_2$, as disulfonate = $C_{16}H_{10}N_2O_2(SO_3H)_2$

Sodium hydrosulfite = $Na_2S_2O_4$ (?) debatable.

$$[C_{16}H_8N_2O_2(SO_3H)_2 + H_2O] - O = C_{16}H_{10}N_2O_2(SO_3H)_2$$
$$Na_2S_2O_4 + O = Na_2SO_3 + SO_2$$
$$\text{or } Na_2S_2O_4 + 2NaOH + O = 2Na_2SO_3 + H_2O.$$

The complete reaction is:

$$2NaOH + C_{16}H_8N_2O_2(SO_3H)_2 + Na_2S_2O_4 = C_{16}H_{10}N_2O_2(SO_3H)_2 + 2Na_2SO_3$$

Standardization of Solutions

Into the clean, dry, graduated 400-c.c. beaker place one drop of phenolphthalein indicator and cover with a ¾-in. layer of kerosene. Care should be used to avoid entrapping air bubbles. The oxygen-saturated water is now siphoned into the beaker below the kerosene. The line of demarcation between the kerosene and the solution is very distinct by the red color produced with the indicator in the alkaline water; thereby a close measurement of the water can be attained. When 250 c.c. of water

has been measured out beneath the kerosene, the alkalinity is neutralized with dilute sulfuric acid from a burette, the tip of which extends below the surface of the solution; 1 c.c. of the indigotin disulfonate solution is then run in beneath the kerosene. The solution is now titrated with the hydrosulfite solution. The tip of the burette must dip beneath the kerosene so that, by constant stirring with the special stirring rod (Fig. 3), any entry of air is avoided. The titration with hydrosulfite first reacts with the dissolved oxygen; as the end point is reached the hydrosulfite decolorizes the indigo disulfonate and the end point is yellow or yellowish white. When this point is reached, the burette is read and noted and 5 c.c. of indigo disulfonate solution is run in, all of the above precautions being taken; this is again followed by titration with the

FIG. 3.

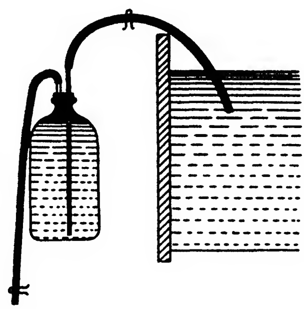


FIG. 4.

hydrosulfite. This operation gives the required relationships between the various solutions.

Assume that the water showed a saturation of 8 mg. per liter for the particular temperature and pressure, and that the titration gave 9 c.c. hydrosulfite standard followed by 5.5 c.c. more, after 5 c.c. of the indigotin disulfonate standard was added. Then 5 c.c. indigotin = 5.5 c.c. hydrosulfite; and 1 c.c. indigotin = 1.1 c.c. hydrosulfite. Also, as 1 c.c. of the indigotin was used at the start, we must correct the first hydrosulfite titration for the 1 c.c. indigotin used, which is 1.1 c.c.

The amount of hydrosulfite then consumed on the dissolved oxygen is, 9.0 c.c. – 1.1 c.c. = 7.9 c.c. Now, 7.9 c.c. hydrosulfite = 8 mg. oxygen per liter, or 1 c.c. hydrosulfite = 8.0 ÷ 7.9 = 1.01 mg. oxygen per liter, when 250 c.c. of the saturated water is titrated. Also, 1 c.c. indigotin disulfonate standard is equivalent to $\frac{1.1 \times 1.01}{4} = \frac{1.11}{4} =$ 0.28 mg. oxygen.

The indigo disulfonate does not deteriorate and may be kept in a well-stoppered bottle. When once standardized, it may be used to check the standard hydrosulfite solution instead of making up aerated water. In

this case, sufficient water should be added to the indigo-disulfonate solution until 1 c.c. exactly equals 0.25 mg. oxygen.

Titration of Mill Solutions

When once the hydrosulfite and indigotin-disulfonate solutions are standardized, the procedure with routine solution titrations is simple. The solution is siphoned over beneath the kerosene into the 400-c.c. beaker until 250 c.c. is obtained, the alkalinity is then neutralized with dilute sulfuric acid, 1 c.c. or less of indigotin disulfonate is added as an indicator, and titration is completed with the hydrosulfite. Following this, the necessary correction is made for the indicator and the result is converted to milligrams of oxygen per liter of solution, or per cent. saturation as may be desired. The kerosene may be used several times by pouring the contents of the beaker into a large bottle, after titration, then siphoning off the kerosene for reuse after sufficient accumulation.

Precautions

After the aeration of the solution in the standardization process, sufficient time must be allowed for all entrapped air bubbles to escape before titration or the end point will "go back" rapidly and erroneous results are obtained.

When stirring the solution during titration, care must be taken not to introduce air into the solution. This stirring is done by revolving the special stirring rod between the thumb and fingers, holding it vertically.

A cover of kerosene should always be kept over the solution.

When mill solutions are used to standardize the hydrosulfite solution, care must be taken that they are thoroughly saturated as they saturate much more slowly than tap or distilled water. It sometimes requires more than an hour to saturate them completely.

The end point in clear solutions is a slight yellow; but if solutions contain certain salts, or are cloudy, the end-point color may be white or milky, or sometimes gray.

All connections through which the standard solution pass must be sealed air-tight. This is best done with shellac.

When neutralizing the alkalinity of the solution for titration, care must be taken that it is just neutral to phenolphthalein. If it is too acid, the titration will be low; if it is too alkaline, the titration will be too high.

Manipulation in the procedure must be as rapid as possible without sacrificing accuracy, for notwithstanding the cover of kerosene, there will be a slow absorption of oxygen through the kerosene.

If the end point is over run, back titration can be made with the standard indigo disulfonate; or, if more desirable, an excess of hydrosulfite solution may be run in and the excess titrated with indigo-disulfonate standard.

Sampling of Mill Solutions

Reasonably clear mill solutions are best sampled by using a bottle, as shown in Fig. 4. This bottle forms part of a siphon, into which a sample may be safely transported to the laboratory. When sampling, the end of the tube that reaches to the bottom of the flask is connected through a pinch cock and tubing to the tank, launder, or other source of solutions to be tested. The tube that just reaches through the cork is also connected to rubber tubing and has a pinch cock. The connections are made as shown and the siphon started by suction. After the bottle is filled with solution, the apparatus is allowed to run for a while to replace any contaminated solutions. The pinch cocks are then closed and the bottle may be transported to the place for titration.

Pulps require settlement before the solutions can be removed for titrations. In this case, it is best to fill a Winchester bottle completely with pulp, close the bottle with its cork, and allow the whole to stand until the solution can be siphoned off.

Examinations made of many operating plant solutions allow the following generalities:

	Per Cent. of Maximum Oxygen Saturation
General circulating plant solutions	7 to 75
Agitator solutions	0 to 50
Leaching-plant effluent	0 to 50
Crowe vacuum operation removes as a rule, one-half of the oxygen contained in its feed.	
Precipitation plant barrens	0
Concentrate treatment agitator solutions	0

We desire to express our appreciation to the Golden Cycle Mining & Reduction Co., Colorado Springs, Colo.; The Homestake Mining Co., Lead, S. Dak.; The United Comstock Mines Co., Comstock, Nev.; and the Empire Mines at Grass Valley, Calif., for special interest and help in this work and to numerous other mills that have assisted in many ways in this undertaking.

DISCUSSION

A. L. Blomfield* and M. F. Dycus, Colorado Springs, Colo. (written discussion).—We have found the Weinig-Bowen method, for the determination of oxygen in solution, of great value in the calculation of oxygen in mill solutions at the Golden Cycle mill. The apparatus, while simple in design, is both rapid and accurate. After becoming accustomed to the operations to be made, a determination may easily be made in two minutes, not including the sampling and measuring of the solution. To date, the oxygen determinations have been made by but two or three men; however, the manipulation is so simple that any

* General Manager, Golden Cycle Mining & Reduction Co.

millman can learn how in a very short time and therefore be able to get a check on any or all solutions at any time.

We had some difficulty with the apparatus, as first made, which calls for a shellac-sealed bottle, for after being used for a time (in some cases several weeks) the shellac softened and allowed the joint to leak. This was probably due to the kerosene contained in the upper portion of the bottle. We have remedied this by making ground-glass connections throughout and mounting the whole apparatus in a stationary cabinet.

The manipulation is the governing factor as to accuracy. After taking a sample into the beaker for titration, all haste should be made, without sacrificing accuracy, to complete the operation. If the solution is allowed to stand, even under a cover of kerosene, it will take up oxygen quite rapidly and give fictitious results. The beaker must be thoroughly dry before using; also, we experienced some difficulty if kerosene was poured violently into beaker; this should be done very gently in order that there may be no possible chance to imprison tiny air bubbles under its layer.

In calculating the percentage of maximum oxygen saturation, after making all titrations, we have found it of some advantage to use a table, which covers our local requirements only. The solution temperature varies but a few degrees in the whole plant so that the table does not need to cover a very wide range. It is fastened to the cabinet door and promotes speed as well as eliminating almost all chance of a misreading.

The ore our solutions work on comes direct from the roasters. The solutions, therefore, take up a great many substances, some one or more of which have made all previously tried methods unreliable and inconsistent. Below is an average week's run of some of the various solutions in the plant. While these vary a great deal, it is probably an actual change in the amount of oxygen in a particular solution rather than any deficiency in the apparatus, as two or more samples taken from the same place at the same time check very closely.

Per Cent. of Maximum Oxygen Saturation

Gold storage. High-grade solution before entering Crowe vacuum system	49.5	49.5	54.1	62.0	53.7	47.0	63.1
Zinc-box feed. High-grade solution after passing Crowe vacuum system	10.5	30.0	7.8	15.0	16.7	6.9	12.3
Zinc-box tails	7.0	10.0	3.2	3.3	5.1	8.4	3.1
Stock tank. Low-grade solution before entering Crowe vacuum system	44.0	44.0	71.6	73.6	60.9	55.6	41.8
Zinc-dust press feed. Low-grade solution after passing Crowe vacuum system	3.5	6.7	3.2	4.9	3.4	1.7	6.1
Zinc-dust press tails	2.9	1.6	2.8	4.1	3.2	3.3	4.5

A. W. Bull, New York, N. Y.—There are two points that might be touched on in the discussion: First, in regard to the oxygen solubility curves, it should be noted that, if a very high degree of accuracy is wanted, the actual atmospheric pressure should be taken. The authors use the average pressure for any given altitude. If there was considerable variation in barometric pressure, it would make a difference in the saturation value of the standards. A difference of 1 in. in the barometer, not unusual at sea-level altitude, corresponds to 800 ft. altitude.

The second point is in regard to the testing of pulps. The authors state that pulps require settlement before testing. There is one case in which this might give misleading results. The pulp in an agitator might contain oxygen that, during settlement, would be consumed by further dissolution of the gold and silver values. The result after settlement would mislead you into thinking there was less oxygen in the agitator than was present under operating conditions.

Milling Practice of American Zinc Co. of Tennessee at Mascot

By Robert Ammon,* Mascot, Tenn.

(Birmingham Meeting, October, 1924)

The milling practice at Mascot, at present, consists of dry crushing to ⅝ in., jigging, fine grinding, and flotation. The ore arrives at the mill from two mines, No. 1 mine shaft being located in the mill proper, and No. 2 mine shaft being situated about 2000 ft. east of the mill. No. 2 mine is served by a coarse-crushing plant and aerial tramway to the mill bins. In jigging the No. 2 mine ore, 50 per cent. of the mill feed is rejected by the jigs as a jig tailing ranging from ⅝ in. to 10 mesh; the balance of this ore, after removing a jig concentrate, is ground to flotation feed. In jigging No. 1 mine ore, approximately 80 per cent. of the mill feed is rejected as a coarse jig tailing, and the balance is ground to flotation feed without the removal of a jig concentrate. The difference in the treatment is due to the fact that No. 2 mine ore carries a higher content of zinc than that from No. 1 mine. Of the total concentrates produced, 30 per cent. is made on jigs and 70 per cent. by flotation. At present, 1350 tons of No. 2 ore and 800 tons of No. 1 ore are treated each 24 hours. The recoveries for a typical week are as follows:

Heads	3.55	Jig concentrates	61.30
Jig tails	0.80	Flotation concentrates	60.60
Flotation tails	0.09	Extraction	86.50

The associated minerals are a straw-colored sphalerite, dolomite, calcite, pyrite, quartz, and a small amount of greenockite, which occurs as a stain and sometimes small crystals along with sphalerite, but is comparatively rare. Pyrite is present in small quantities, usually less than 0.5 per cent.; quartz occurs in bands a few inches thick. A complete analysis of the ore is as follows:

	Per Cent.		Per Cent.
Calcium carbonate	48.11	Zinc sulfide	5.43
Magnesium carbonate	35.36	Cadmium sulfide	Nil
Silica	8.73	Lead sulfide	Nil
Alumina	1.04		
Iron oxide	1.33	Total	100.00

* Superintendent of Mills, American Zinc Co. of Tennessee.

Location of Mill

The main concentrator is located at the shaft of No. 1 mine, which at present is producing low-grade ore. The flotation plant and concentrate-drying plant are located in separate buildings approximately 100 yd. from the main mill.

Coarse-crushing Plants

Each of the two shafts is served by a crushing plant consisting of No. 8 bronze gyratory crusher and a 48-in. horizontal Symons disk crusher reducing the ore to 1$\frac{5}{16}$ in. The mine-run ore is hoisted in 5-ton balanced skips to a 20-ton hopper, from which a 42-in. Stephens & Adamson pan feeder, on 10-ft. centers, feeds the ore into a No. 8 gyratory crusher; the discharge of this is fed by a conveyor to a Symons crusher and then conveyed to the storage bin. As the capacity of the gyratory primary breaker in reducing to 4$\frac{1}{2}$ in. exceeds that of the Symons, which reduces to 1$\frac{5}{16}$ in., the operation of the feeder to the gyratory is intermittent. This is controlled by a pawl and ratchet gear which is regulated by the operator.

The size of the ore fed to the gyratory crusher is often greater than the crusher will receive, which necessitates breaking by sledging or drilling and popping on top of the crusher. A Jackhamer is always available for these large boulders.

The gyratory crushers are equipped with manganese concaves and smooth manganese mantles. The record of mantles and concaves follows:

	Number Worn Out	Average Cost	Tons Crushed	Average Cost per 100 Tons, Cents
Lower concaves	11	$211.39	417,225	5.667
Mantles	4	$340.00	570.658	5.958

This cost is for corrugated mantles. Since the adoption of smooth mantles none have been worn out, but the steel cost per ton crushed should be less than that shown for corrugated mantles. The gyratory makes 150 strokes per minute.

Only the lower concaves are replaced; in 10 years of operation, no upper concaves have worn out. A 16 T Yale & Towne triplex chain block suspended on a steel craneway from a traveling carriage serves the gyratories for repairs.

The discharge of the primary breakers is conveyed to a 48-in. horizontal Symons crusher equipped with manganese disks. At No. 1 shaft, the Symons discharge is conveyed directly to the mill; and at No. 2 shaft, to the tramway loading bin.

AVERAGE COST OF BELTING FOR ELEVATING SYMONS CRUSHER DISCHARGE
110-FT. BELT

	Number of Belts	Cost	Tonnage	Days Service	Cost per 100 Tons Elevated, Cents
Diamond Rubber Co. Portage belt...	6	$279.58	280,809	309	9.96
Goodyear Rubber Co. Compass belt.	2	$431.18	436,784	420	9.65

AVERAGE COST OF BELTING FOR CONVEYING GYRATORY CRUSHER DISCHARGE

	Number of Belts Average	Cost	Tons Conveyed	Days Service	Cost per 100 Tons Conveyed, Cents
Diamond Rubber Co. Diamond brand	28	$118.43	89,623	88	13.92
Goodyear Co. Blue-streak............	3	$231.49	229,842	257	10.93

The product of each of the crushers is as follows:

Size, Diam. of Round Hole, Inches	Gyratory Discharge, Per Cent.	Symons Discharge, Per Cent.	Size, Diam. of Round Hole, Inches	Gyratory Discharge, Per Cent.	Symons Discharge, Per Cent.
On 5	7.9		On 1½	3.5	10.9
On 4½	6.1		On 1¼	3.9	16.4
On 4	9.4		On 1	4.6	12.7
On 3½	12.7		On ½	7.4	19.8
On 3	9.0		Through ½	10.6	22.3
On 2½	10.4				
On 2	10.0		Total......	100.0	100.0
On 1¾	4.5	17.9			

When doing this work, each crushing plant has a capacity of 110 tons per hour, the capacity being limited by the Symons crusher. The average tonnage crushed by a set of disks is 450,000 tons. While the

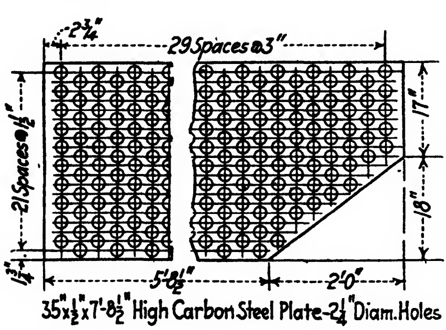


FIG. 1.—GRIZZLY SCREEN FEEDING SYMONS DISK.

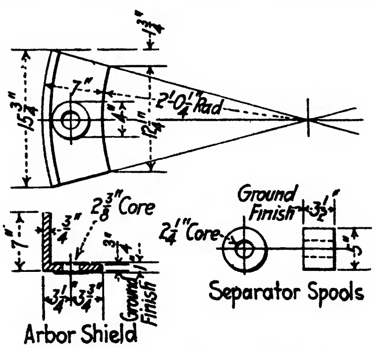


FIG. 2.—MANGANESE-STEEL PROTECTING PLATES AND SHIELDS FOR SYMONS DISK CRUSHER.

Symons crushers, as operated today, give excellent service, four changes, as follows, were required in the machine as furnished before satisfactory operating was obtained:

Discarding the dart oil wipers and installing the flat brass wiper. Equipping heads with manganese-steel protecting plates to prevent excessive wear (see Fig. 2).

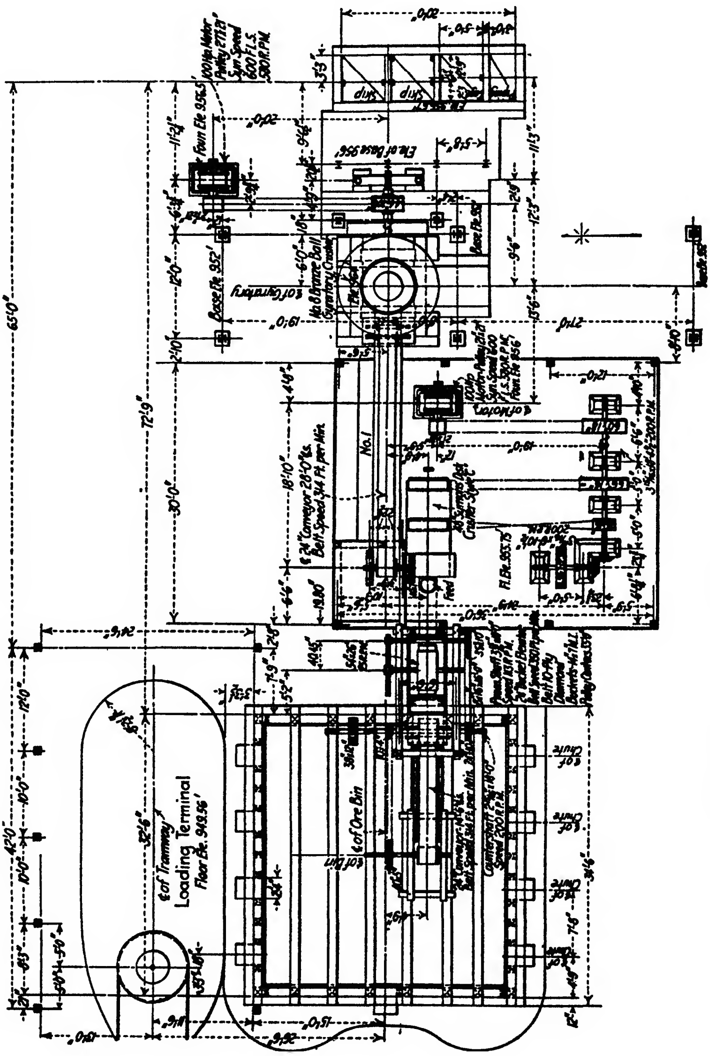


FIG. 3.—PLAN OF NO. 2 CRUSHING PLANT, AS INSTALLED.

Replacing cast-iron ball of inner shaft with steel ball. All of the shafts furnished with cast-iron balls failed by the shaft pulling out of the ball; no trouble has been experienced since using a steel ball.

Installing a dust ring on the outer shaft just clearing the main base, which prevents particles of ore getting into the base of the machine and contaminating the circulating oil.

The chute feeding the Symons crusher has for its bottom (see Fig. 1) a manganese-steel plate with 2-in. round holes. This serves as a grizzly to remove fine ore and is especially useful when very wet ore is hoisted. Ordinarily, the moisture content of the mine-run ore is under 2 per cent. but when very wet ore is hoisted, because of water trouble in the skip pockets, the grizzly screen removes enough of the sticky fines to prevent choking the disk crusher.

Suspended about 8 in. above the conveyor belt feeding each Symons crusher is a 54-in. diameter Type SA No. 4 lifting magnet, to catch tramp steel. These magnets are the only protection these crushers have against iron and catch many steel drill bits, hammer heads, etc. Both outer and

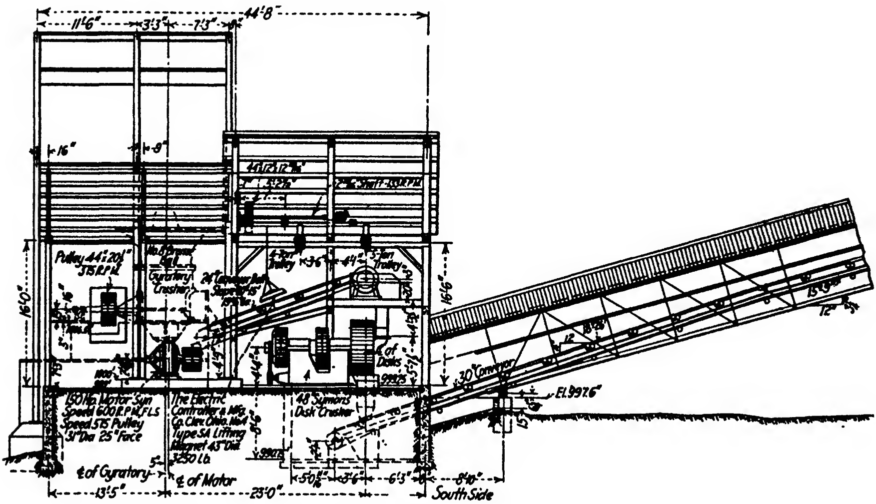


Fig. 4.—Elevation of No. 1 crushing plant, as installed.

inner shafts have been broken at different times by a bit or hammer head passing the magnet because it was covered too deeply with ore. To reduce this liability, the eccentric flywheel is driven with an 8-in. belt instead of a 12-in., as originally installed; this allows the belt to slip on the pulley should a piece of steel get between the disks. The manganese-steel plates and spools used for protecting the bolts and heads of the Symons crusher are shown in Fig. 2.

Manganese-steel feed spouts are also used and last about 8 months.

Each Symons crusher is served by a set of 4- and 5-ton Yale & Towne triplex chain blocks, each suspended on an I-beam crawl.

The cost of steel for the disks is approximately $0.034 per 100 tons crushed. Figs. 3 and 4 show plan of No. 2 crushing plant and an elevation of No. 1 crushing plant as originally installed.

CRUSHING AND TRAMMING COSTS, IN CENTS, PER TON HANDLED

	LABOR	SUPPLIES	REPAIRS	POWER	TOTAL
Coarse crushing	0.92	0.29	2.59	0.75	4.55
Aine crushing	1.02	0.15	1.17	1.47	3.81
Ferial tramming	3.07	0.17	0.39	0.10	3.73

AERIAL TRAMWAY

The product of the crushing plant at No. 2 shaft is transported to the mill bin by a Bleickert aerial tramway, over a distance of 2000 ft. This tramway was constructed, in 1914, by the American Steel & Wire Co. The operation requires two men at each terminal to attach the loaded and empty buckets. The line carries 18 buckets, each holding 1600 lb. of ore.

TRAMWAY CABLE DATA

	NUMBER OF CABLES	AVERAGE COST	AVERAGE DAYS	AVERAGE TONS TRAMMED	AVERAGE COST PER 100 TONS
5/8-in. haulage 6 × 7 strand hemp core Lang lay crucible steel	5	$ 383.36	564	519,885	$0.07374
1 1/2-in. track cable locked-coil 7 × 12 × 21 × 25 strand	3	1611.99	956	924,159	0.17433
1-in. track cable locked-coil 7 × 16 strand	1	734.27	1308	1,156,543	0.06350

FINE-CRUSHING DEPARTMENT

This consists of two sets of 54 by 20 in. Garfield rolls, operating in closed circuit with 5/8-in. screens; each set as a unit. Formerly the screens used were four 4 by 8 ft. trommels to each unit but at present a No. 2 Mitchell vibrating screen replaces the four trommels on the low-grade unit. The undersize from this screen goes directly to jigs, whereas the undersize of the trommels (5/8-in. round holes) treating the higher grade ore is conveyed to a 2500-ton storage bin, from which it is drawn as regular mill feed.

The operating of the Mitchell screen has been highly satisfactory; it has averaged 55 tons undersize per hour with few repairs outside of screen cloth.

Until the last few years tire-steel shells were used for this crushing, being shrunk on to the cores. This was done by mounting the shell on the cores, pulling up the loose core as much as possible, when cold, and then heating the shell with a circular oil burner until the cores could be pulled an additional 1/2 in. on either side. No difficulty was had from the steel cracking or stretching enough to loosen when in operation. After testing out the manganese steel made by Taylor-Wharton Iron & Steel Co., it was decided to adopt manganese steel for this work entirely. These shells are not shrunk on when new but are pulled as tight as possible and the core bolts tightened each week when the shells are warm from grinding. After these shells become half worn, they are shrunk upon the cores and worn out. New shells are 5 in. thick and last from 1 to 1 1/2 years.

Comparative Average Costs of Roll Shells

	Number of Sets Averaged	Cost	Tonnage	Days Service	Cost per 100 Tons Crushed
Manganese steel, Taylor-Wharton........	3	$1255.18	316,712	374	$0.3963
Latrobe steel, Railway Spring Steel Co...	16	1103.59	89,809	94	1.3535
Tire steel, Midvale Steel Co.............	13	738.50	103.430	106	0.7927

The rolls are operated without shims between the sliding bearing and the fixed bearing, the wear on the shells being taken up by the tension-rod nut. Frequently when the roll feed becomes coarser than 1⅜-in. because of the wearing of the Symons disks, the rolls refuse to nip the coarse dolomite. This is overcome by burning four ridges about ½ in. wide and ¼ in. deep across the face of each shell with an acetylene torch. This burning is required about once in 8 weeks and only when the feed becomes coarse.

Each roll-feed conveyor is equipped with an Electric Controller & Mfg. Co's. lifting magnet for the removal of tramp iron and steel. These magnets often pick up shims and 2¼-in. hexagonal nuts that come from the Symons crushers.

For changing shells, a 10-ton hand-power traveling Whiting Foundry crane serves both sets of rolls.

Average Cost of Belting for Conveying Minus ⅝-in. Material

	Number of Belts Averaged	Cost	Tons Conveyed	Days Service	Cost per 100 Tons Conveyed
Diamond Rubber Co. Diamond Brand.....	9	$271.76	1,038,809	568	$0.0261

Average Cost of Elevating Roll Discharge

	Number of Belts Averaged	Cost	Tons Conveyed	Days Service	Cost per 100 Tons Conveyed
Diamond Rubber Co. Portage Brand..........................	11	$293.15	278,396	289	$0.1053
Goodyear Rubber Co. Compass Brand	3	434.29	363,535	378	0.1194
Manhattan Co. Endurance Brand..	1	404.42	339,637	389	0.1191

Crusher Bearings

So-called XXXX nickel babbitt is used in all heavy-duty bearings. The shaft bearings of the rolls have been rebabbitted once in 9 years.

The eccentric of the gyratories lasts from 3 to 5 months, while main-shaft bearings and the inner ball of the Symons average about 2 years' service.

The use of Promet metal, manufactured by American Crucible Products Co., was not successful in the gyratory and the Symons crushers.

Jigging Department

From the storage bin No. 2 mine ore is drawn on a 24-in. belt conveyor served by a Merrick weightometer. The ore is conveyed to an elevator

through a sampler and, after fresh water is added to the boot, is elevated on to the rougher jigs. Fig. 5 shows cross-section of feeder and belt under the storage bin.

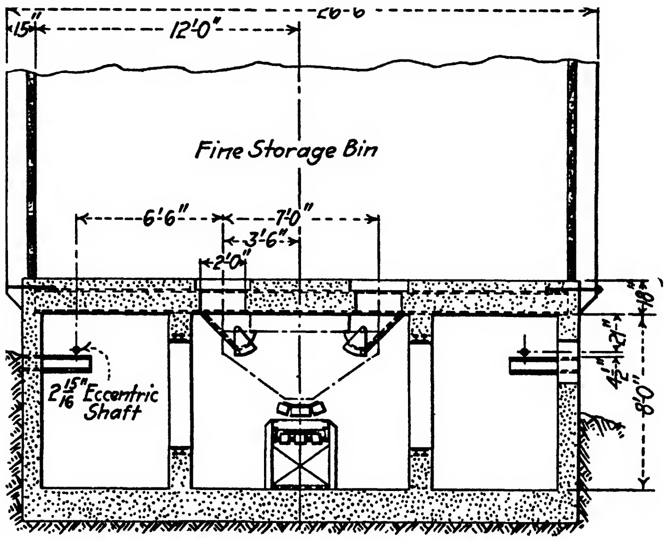


FIG. 5.—CROSS-SECTION OF FEEDER UNDER STORAGE BIN.

SCREEN ANALYSIS OF NO. 2 ORE

Screen Size	Opening, Milli-meters	Solids		Zinc			
		Per Cent.	Cumulative Per Cent.	Assay Per Cent. Zinc	Cumulative Assay Per Cent. Zinc	Per Cent. Total Zinc	Cumulative Per Cent. Zinc
On 3 mesh	6.656	23.1	23.1	3.62	3.62		
On 6 mesh	3.328	26.0	49.1	2.63	2.36	18.9	32.1
On 10 mesh	1.664	15.9	65.0	3.71	2.69	16.3	48.4
On 20 mesh	0.832	10.6	75.6	4.79	2.98	14.0	62.4
On 35 mesh	0.416	7.1	82.7	5.74	3.22	11.3	73.7
Through 35 mesh		17.3	100.0	5.54	3.62	26.3	100.0
Total		100.0	100.0	3.62	3.62	100.0	100.0

The ore, without any preliminary treatment, is jigged on a six-cell Cooley type Harz jig, making hutch, middling, and tails. The tails are dewatered on stationary screens using 1 by ⅛ in. slotted punched plates (see Fig. 6); the oversize, practically free from slime, is rejigged on three-cell jigs of the same type making tails and hutch middling.

The jigs originally were built of pine and last from 7 to 12 years. As these are replaced, cypress is used instead of pine. Fig. 7 shows detail

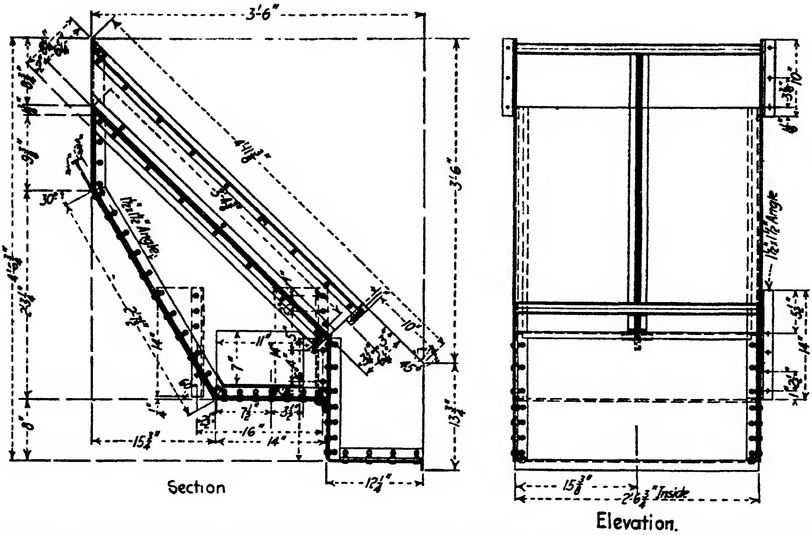


FIG. 6.—STATIONERY DEWATERING SCREEN FOR DESLIMING ROUGHER JIG TAILS.

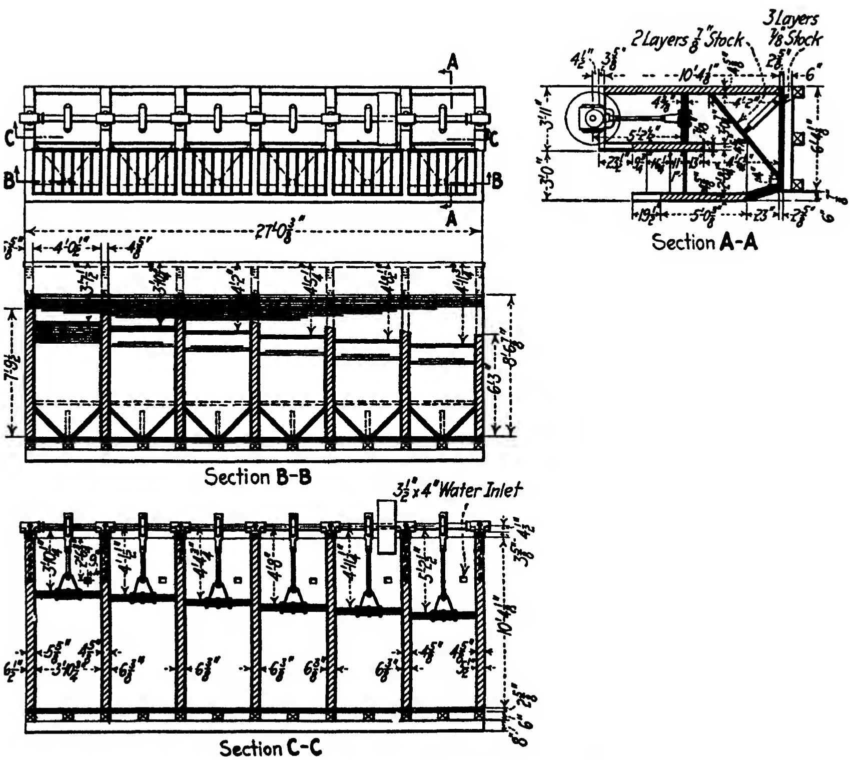


FIG. 7.—DETAILS OF SIX-CELL ROUGHER JIG.

construction of the six-cell rougher jigs. Solid non-adjustable eccentrics of local design, made by Power & Mining Machinery Co., are used on these jigs with plungers so placed that top of plunger is 1½ in. above the top of the sieve at the highest point of movement of the eccentric.

	Rougher Jigs	Bull Jigs
R. P. M.	110	82
Stroke, first cell, inches	1⅝	2
Stroke, second cell, inches	1⅝	1¾
Stroke, third cell, inches	1½	1½
Stroke, fourth cell, inches	1½	
Stroke, fifth cell, inches	1⅜	
Stroke, sixth cell, inches	1⅜	

The Joplin cast-iron grates formerly used on these jigs have been replaced by punched-steel plates. The roughers are equipped with No. 14 steel slotted plates with slots 1 in. long and ⅛ in. wide (see Fig. 8). On the bull jigs, which make all their middling through the hutch, No. 10 steel plates are used having ½-in. round holes. Punched slotted plates average 3 to 4 months service and the ½-in. round-hole bull jig screens last a year.

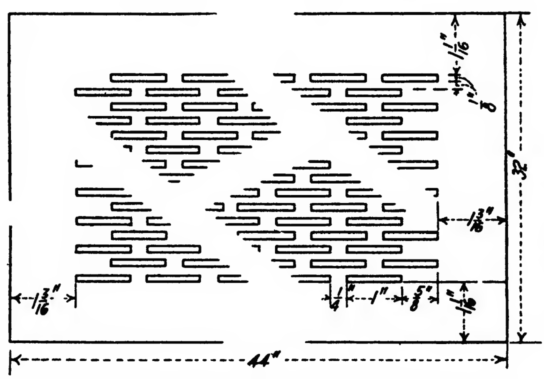


Fig. 8.—Punched plate used as jig sieves.

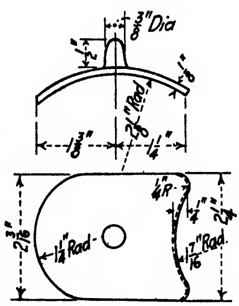


Fig. 9.—Manganese-steel lip for jig hutch discharge gate.

The sieves are held in place by frames made of 1½ by 3½ in. pine with crossbars 1 in. wide, spaced 4½ in. on centers. The crossbars are dovetailed with the main frame to prevent twisting. The screens are fastened to the frames with sixpenny nails.

The roughers make their own bedding of sphalerite, the excess being drawn off, on the first two cells, by side cup draws and, on the last four cells, through the regular middling discharge, or "chatters," which are continuous in operation. As no coarse free mineral is in the feed to the

bull jigs, bedding is added to them in the form of round-plate punchings ¼ to ½ in. thick and ⅝ to ¾ in. in diameter. A bed of about 1 in. in depth is kept on the bull-jig cells. The sieve screen on all jigs is elevated 1 in. at the tail-board end of the cells.

The middling draw, or "chatter," on the last four cells of the rougher jigs consists of a steel plate across the tail board of each cell with 1-in. round holes, usually four, placed 3½ in. above the screen and equally spaced across the length of the plate. One or more of these openings may be closed off temporarily in case of low-grade ore, in order to allow bedding to build up. In case too much bedding is accumulated on the last four cells, it is removed with a shovel. This is the exception, however, as the first two cells, if properly operated, will regulate the bedding to the balance of the jig. Excess bedding (sphalerite) removed from the cells joins the continuous middling discharge of the jigs, no attempt being made to segregate a coarse concentrate, although bedding so removed assays better than 50 per cent. zinc.

The hutch discharge on the jigs is continuous through 2-in. molasses gates equipped with manganese-steel lips. On sand, these gates allow close regulation of the water producing a dense discharge. Fig. 9 shows manganese lip.

With a feed of 28 tons per hour per jig, the average depth of bed on the cells of the jigs is as follows:

	Rougher Jig, Inches	Bull Jig, Inches		Rougher Jig, Inches	Bull Jig, Inches
Cell 1	12	10	Cell 4	11	...
2	12	8½	5	10	...
3	11	6¾	6	9	...

The material required to build one six-cell rougher jig is 880 pieces 2 in. by 6 in. by 16 ft. cypress, 6 pieces 8 in. by 8 in. by 16 ft. pine, 6 pieces 6 in. by 6 in. by 12 ft. pine, 100 pieces 1 in. by 12 in. by 16 ft. pine, 12 pieces 2 in. by 12 in. by 16 ft. pine, 14 kegs 20 penny nails, 3 kegs 30 penny nails, 2 kegs 8 penny nails.

Average Jigging Department Costs, in Cents per Ton Milled

Labor	2.79
Supplies	0.35
Repairs	1.63
Power	1.01
Total	5.78

Rougher-Jig Hutch

Screen Size	Size, in Millimeters	Solids: Per Cent. Weight	Solids: Cumulative Per Cent. Weight	Zinc: Assay Per Cent. Zinc	Zinc: Cumulative Assay, Per Cent.	Zinc: Per Cent. Total Zinc	Zinc: Cumulative Per Cent. Total Zinc
On 3 mesh	6.656						
On 6 mesh	3.328	1.6	1.6	28.20	28.20	4.4	4.4
On 10 mesh	1.664	5.3	6.9	24.10	25.00	12.3	16.7
On 20 mesh	0.832	14.1	21.0	12.90	16.85	17.6	34.3
On 35 mesh	0.416	20.3	41.3	9.10	13.05	17.8	52.1
On 65 mesh	0.208	19.7	61.0	8.10	11.42	15.4	67.5
On 100 mesh	0.147	13.1	74.1	8.00	10.80	10.2	77.7
On 150 mesh	0.104	9.2	83.3	8.20	10.55	7.3	85.0
On 200 mesh	0.076	7.8	91.1	9.20	10.40	6.9	91.9
Through 200 mesh	0.076	8.9	100.0	9.50	10.35	8.1	100.0
Total		100.0	100.0	10.35	10.35	100.0	100.0
Original sample				10.75			

Total Middling from Rougher and Bull Jigs

Screen Size	Size, Millimeters	Solids: Per Cent. Weight	Solids: Cumulative Per Cent. Weight	Zinc: Assay Per Cent. Zinc	Zinc: Cumulative Assay, Per Cent.	Zinc: Per Cent. Total Zinc	Zinc: Cumulative Per Cent., Total Zinc
On 3 mesh	6.656	38.1	38.1	6.90	6.90	44.0	44.0
On 6 mesh	3.328	39.4	77.5	6.25	6.66	41.3	85.3
On 10 mesh	1.664	14.4	91.9	4.32	6.22	10.4	95.7
On 20 mesh	0.832	4.7	96.6	2.92	6.05	2.2	97.9
On 35 mesh	0.416	1.8	98.4	2.80	6.01	0.8	98.7
On 65 mesh	0.208	0.8	99.2	3.12	5.98	0.4	99.1
On 100 mesh	0.147	0.3	99.5	3.40	5.97	0.2	99.3
On 150 mesh	0.104	0.2	99.7	4.40	5.97	0.2	99.5
On 200 mesh	0.076	0.1	99.8	5.95	5.97	0.2	99.7
Through 200 mesh	0.076	0.2	100.0	8.20	5.97	0.3	100.0
Total		100.0	100.0	5.97	5.97	100.0	100.0
Original sample				5.75			

STATIONARY DEWATERING SCREEN UNDERSIZE

Screen Size	Size, Millimeters	Solids		Zinc			
		Per Cent. Weight	Cumulative Per Cent. Weight	Assay Per Cent. Zinc	Cumulative Assay, Per Cent.	Per Cent. Total Zinc	Cumulative Per Cent. Total Zinc
On 3 mesh	6.656	2.1	2.1	0.70	0.70	1.0	1.0
On 6 mesh	3.328	11.0	13.1	0.77	0.76	5.8	6.8
On 10 mesh	1.664	37.9	51.0	0.90	0.87	23.3	30.1
On 20 mesh	0.832	19.3	70.3	0.55	0.78	7.9	38.0
On 35 mesh	0.416	5.9	76.2	0.55	0.77	2.2	40.2
On 65 mesh	0.208	2.2	78.4	0.90	0.78	1.4	41.6
On 100 mesh	0.147	1.3	79.7	0.82	0.78	0.8	42.4
On 150 mesh	0.104	1.7	81.4	1.20	0.79	1.4	43.8
On 200 mesh	0.076	2.0	83.4	2.30	0.83	3.1	46.9
Through 200 mesh	0.076	16.6	100.0	4.62	1.47	53.1	100.0
Total		100.0	100.0	1.47	1.47	100.0	100.0

Original sample.. 1.57

BULL JIG TAILS

Screen Size	Size, Millimeters	Solids		Zinc			
		Per Cent. Weight	Cumulative Per Cent. Weight	Assay Per Cent. Zinc	Cumulative Assay, Per Cent.	Per Cent. Total Zinc	Cumulative Per Cent., Total Zinc
On 3 mesh	6.656	60.1	60.1	0.75	0.75	61.5	61.5
On 6 mesh	3.328	35.0	95.1	0.70	0.73	33.2	94.7
On 10 mesh	1.664	4.3	99.4	0.57	0.73	3.3	98.0
On 20 mesh	0.832	0.3	99.7	0.85	0.73	0.4	98.4
On 35 mesh	0.416	0.1	99.8	3.52	0.73	0.5	98.9
Through 35 mesh	0.208	0.2	100.0	4.10	0.74	1.1	100.0
Total	0.104	100.0	100.0	0.74	0.74	100.0	100.0

Original assay.. 0.77

The bull jigs are practically scavengers on the deslimed rougher jig tails and reduce their feed 0.3 per cent. zinc.

The lower grade ore is jigged on five-cell rougher jigs, making a hutch product and tail. The tails are deslimed over the same type of screen as used on the higher grade ore and, after desliming, join the bull-jig tails at the tailing elevator. The hutch and dewatering screen undersize from the low-grade ore join the same products from the higher grade ore for further treatment.

The coarse tails are elevated by a tandem belt elevator and flumed to the loading station at the railroad, where they are loaded, as made, into 50-ton railroad cars. The straight mill tail is sold as railroad ballast,

and several other rock products, such as roofing gravel and concrete stone, are produced by screening out various sizes at the loading station while loading the cars. The faces of the pulley are lagged with conveyor belting with a 3⁄16-in. rubber cover to decrease the slippage of the elevator belt.

Middling Circuit

The middlings from the rougher and bull jigs are dewatered in a 6-ft. Allen cone and elevated to a No. 1 type Mitchell vibrating screen using 3-mesh No. 9 wire cloth, the oversize going to a set of 43½ by 16 in. Garfield rolls in closed circuit with the screen. Manganese-steel shells have not been as successful in these wet rolls as the tire steel, because of the cross corrugating and cupping of the shells. Tire steel wears evenly in this work and makes cheaper operating.

Average Cost of Wet Crushing Shells

	Number of Sets Average	Cost	Tons	Days	Cost per 100 Tons Milled
Midvale tire steel	7	$456.37	400,945	236	$0.1138
Latrobe steel	2	467.28	267,106	149	0.1749
Taylor-Wharton manganese steel	1	952.29	584,846	369	0.1630

The average cost of elevator belting for wet elevators is approximately 0.12 cents per ton milled, all costs being calculated to tons mill feed. All elevators are 22 in. wide seven-ply equipped with No. 10 steel cups spaced 16 in. on centers made in the local shops. For scabs, old belting is cut into pieces about 1½ by 6 in. and placed between cups and belts.

Fine-jigging Section

The undersize of the Mitchell screen is sent directly to a four-cell "chat" jig without dewatering. This jig produces a tailing for flotation grinding and a rich hutch product to be further cleaned. The smittem, or hutch, from all rougher jigs, to which has been added the hutch from the chat jig, is dewatered and treated on a four-cell cleaner jig, producing a clean jig concentrate and a tailing for flotation grinding. The jig concentrates are held in the hutch and drawn off every 2 hours and trammed to the storage bin. Both jigs operate at 200 r.p.m. with a ⅝-in. stroke on the first two cells, ½-in. stroke on the third cell, and ⅜-in. stroke on the last cell. Sieves are the same as are used on the rougher jigs and cup draws are used for regulating the bedding, which is built up from the mineral in the feed to each jig.

Depth of Sand Beds on Fine Jigs

Cell Number	Cleaner Jig, Inches	Chat Jig, Inches
1	10½	9¾
2	9¾	8¾
3	8½	8½
4	7¼	7½

CLEANER-JIG FEED

Screen Size	Size, Millimeters	Solids		Zinc			
		Per Cent. Weight	Cumulative Per Cent. Weight	Assay, Per Cent. Zinc	Cumulative Assay, Per Cent.	Per Cent. Total Zinc	Cumulative Per Cent. Total Zinc
On 3 mesh	6.656	1.0	1.0	5.10	5.10	0.4	0.4
On 6 mesh	3.328	2.5	3.5	24.00	18.50	4.6	5.0
On 10 mesh	1.664	15.8	19.3	19.90	19.60	23.9	28.9
On 20 mesh	0.832	26.1	45.4	14.00	16.40	27.7	56.6
On 35 mesh	0.416	26.5	71.9	11.10	14.50	22.4	79.0
On 65 mesh	0.208	17.0	88.9	9.60	13.50	12.4	91.4
On 100 mesh	0.147	6.2	95.1	9.70	13:25	4.6	96.0
On 150 mesh	0.104	2.6	97.7	10.40	13.20	2.1	98.1
On 200 mesh	0.076	1.0	98.7	11.50	13.18	0.9	99.0
Through 200 mesh	0.076	1.3	100.0	10.60	13.14	1.0	100.0
Total		100.0	100.0	13.14	13.14	100.0	100.0
Original sample				13.30			

CLEANER-JIG TAILS

Screen Size	Size, Millimeters	Solids		Zinc			
		Per Cent. Weight	Cumulative Per Cent. Weight	Assay, Per Cent. Zinc	Cumulative Assay, Per Cent.	Per Cent. Total Zinc	Cumulative Per Cent. Total Zinc
On 3 mesh	6.656	1.8	1.8	2.15	2.15	0.7	0.7
On 6 mesh	3.328	2.8	4.6	2.70	2.56	1.3	2.0
On 10 mesh	1.664	15.5	20.1	4.30	3.89	11.3	13.3
On 20 mesh	0.832	24.8	44.9	4.75	4.36	20.0	33.3
On 35 mesh	0.416	22.3	67.2	6.10	4.95	23.1	56.4
On 65 mesh	0.208	17.7	84.9	6.90	5.35	20.7	77.1
On 100 mesh	0.147	7.9	92.8	7.90	5.56	10.6	87.7
On 150 mesh	0.104	5.6	98.4	8.80	5.82	9.5	97.2
On 200 mesh	0.076	0.3	98.7	10.30	5.84	0.7	97.9
Through 200 mesh	0.076	1.3	100.0	9.50	5.89	2.1	100.0
Total		100.0	100.0	5.89	5.89	100.0	100.0
Original sample				5.90			

Cleaner-jig Concentrates

Screen Size	Size, Millimeters	Solids		Zinc			
		Per Cent. Weight	Cumulative Per Cent. Weight	Assay, Per Cent. Zinc	Cumulative Assay, Per Cent.	Per Cent. Total Zinc	Cumulative Per Cent. Total Zinc
On 3 mesh	6.656	0.0					
On 6 mesh	3.328	11.8	4.8	61.10	61.10	11.8	11.8
On 10 mesh	1.664	47.0	58.8	61.50	61.40	47.2	59.0
On 20 mesh	0.832	29.4	88.2	62.50	61.80	30.0	89.0
On 35 mesh	0.416	7.0	95.2	58.60	61.60	6.7	95.7
On 65 mesh	0.208	3.2	98.4	49.80	61.30	2.6	98.3
On 100 mesh	0.147	1.1	99.5	45.80	61.22	0.8	99.1
On 150 mesh	0.104	0.3	99.8	44.60	61.22	0.7	99.8
On 200 mesh	0.076	0.1	99.9	45.00	61.22	0.1	99.9
Through 200 mesh	0.076	0.1	100.0	50.60	61.22	0.1	100.0
Total		100.0	100.0	61.22	61.22	100.0	100.0

Original sample.......... 60.90

Chat-jig Feed

Screen Size	Size, Millimeters	Solids		Zinc			
		Per Cent. Weight	Cumulative Per Cent. Weight	Assay, Per Cent. Zinc	Cumulative Assay, Per Cent.	Per Cent. Total Zinc	Cumulative Per Cent. Total Zinc
On 6 mesh	3.328	3.9	3.9	3.45	3.45	2.5	2.5
On 10 mesh	1.664	34.4	38.3	5.25	5.07	33.4	35.9
On 20 mesh	0.832	28.1	66.4	5.15	5.10	26.6	62.5
On 35 mesh	0.416	21.2	87.6	5.67	5.23	22.1	84.6
On 65 mesh	0.208	9.4	97.0	6.70	5.40	11.6	96.2
On 100 mesh	0.147	2.1	99.1	7.07	5.42	2.7	98.9
On 150 mesh	0.104	0.6	99.7	7.20	5.43	0.8	99.7
On 200 mesh	0.076	0.2	99.9	7.00	5.44	0.2	99.9
Through 200 mesh	0.076	0.1	100.0	5.85	5.44	0.1	100.0
Total		100.0	100.0	5.44	5.44	100.0	100.0

Original sample.......... 5.17

CHAT-JIG TAILS

Screen Size	Size, Millimeters	Solids		Zinc			
		Per Cent. Weight	Cumulative Per Cent. Weight	Assay, Per Cent. Zinc	Cumulative Assay, Per Cent.	Per Cent. Total Zinc	Cumulative Per Cent. Total Zinc
On 3 mesh	6.656						
On 6 mesh	3.328	4.4	4.4	0.82	0.82	2.5	2.5
On 10 mesh	1.664	37.2	41.6	0.72	0.72	18.3	20.8
On 20 mesh	0.832	20.9	62.5	0.60	0.69	8.6	29.4
On 35 mesh	0.416	13.0	75.5	0.75	0.70	6.7	36.1
On 65 mesh	0.208	7.8	83.3	1.35	0.76	7.2	43.3
On 100 mesh	0.147	3.8	87.1	2.57	0.84	6.7	50.0
On 150 mesh	0.104	2.3	89.4	4.67	0.94	7.3	57.3
On 200 mesh	0.076	2.7	92.1	5.92	1.07	11.0	68.3
Through 200 mesh	0.076	7.9	100.0	5.85	1.46	31.7	100.0
Total		100.0	100.0	1.46	1.46	100.0	100.0
Original sample				1.65			

CHAT-JIG HUTCH

Screen Size	Size, Millimeters	Solids		Zinc			
		Per Cent. Weight	Cumulative Per Cent. Weight	Assay, Per Cent. Zinc	Cumulative Assay, Per Cent.	Per Cent. Total Zinc	Cumulative Per Cent. Total Zinc
On 6 mesh	3.328	7.8	7.8	52.7	52.7	11.4	11.4
On 10 mesh	1.664	41.0	48.8	45.6	46.7	51.5	62.9
On 20 mesh	0.832	16.1	64.9	25.4	41.5	11.3	74.2
On 35 mesh	0.416	7.7	72.6	16.2	38.8	3.5	77.7
On 65 mesh	0.208	5.2	77.8	20.6	37.5	3.0	80.7
On 100 mesh	0.147	4.1	81.9	32.6	37.4	3.7	84.4
On 150 mesh	0.104	3.2	85.1	39.2	37.4	3.4	87.8
On 200 mesh	0.076	3.6	88.7	38.0	37.4	3.8	91.6
Through 200 mesh	0.076	11.3	100.0	26.4	36.2	8.4	100.0
Total		100.0	100.0	36.2	36.2	100.0	100.0
Original sample				36.8			

FINE-GRINDING DEPARTMENT

The dewatered chat-jig and cleaner-jig tails, together with the rougher-jig dewatering-screen undersize, is reduced to 20 per cent. plus 100-mesh by five mills, only four of which are operated simultaneously. The grinding-mill feed is the spigot of two 8-ft. Allen cones containing 75 per cent. solids and of the following fineness.

SCREEN ANALYSIS OF GRINDING-PLANT FEED

Screen Size	Size, Millimeters	Solids		Zinc			
		Per Cent. Weight	Cumulative Per Cent. Weight	Assay, Per Cent. Zinc	Cumulative Assay, Per Cent.	Per Cent. Total Zinc	Cumulative Per Cent. Total Zinc
On 3 mesh	6.656	1.0	1.0	0.20	0.20	0.6	0.6
On 6 mesh	3.328	5.5	6.5	3.50	3.00	5.7	6.3
On 10 mesh	1.664	40.1	46.6	2.00	2.13	23.6	29.9
On 20 mesh	0.832	21.1	67.7	2.70	2.31	16.8	46.7
On 35 mesh	0.416	14.2	81.9	4.35	2.63	18.2	64.9
On 65 mesh	0.208	8.7	90.6	5.60	2.95	14.3	79.2
On 100 mesh	0.147	4.1	94.7	6.20	3.08	7.5	86.7
On 150 mesh	0.104	2.6	97.3	7.30	3.20	5.5	92.2
On 200 mesh	0.076	0.7	98.0	8.40	3.26	2.2	94.4
Through 200 mesh	0.076	2.0	100.0	10.10	3.40	5.6	100.0
Total		100.0	100.0	3.40	3.40	100.0	100.0
Original sample.				3.70			

This material is elevated and distributed to any of the five mills operating, two of which are equipped with model D S D 8 by 25 ft. Dorr duplex classifiers in closed circuit. The discharge of the mills without classifiers is elevated by a 4-in. Wilfley pump and can be sent to the feed launder of either classifier, as only one classifier is needed most of the time.

DATA ON WILFLEY PUMP FOR ELEVATING GRINDING-MILL DISCHARGE

Size of pump	No. 4
Revolutions per minute	1080
Drive	10-in. belt
Gallons per minute	150
Ratio water to solids	1 to 1
Dry tons per hour	20
Discharge lift, feet	30
Pressure at pump, pounds	18–20
Size of pipe, inches	4
Length of pipe, feet	30
Intake head above pump shaft, inches	20
Size of pipe, inches	6
Length of pipe, inches	6
Mesh	2 per cent. + 20 50 per cent. + 100
Specific gravity of solids	3.00
Character	90 per cent dolomite 10 per cent sphalerite

The pump is fed through a concrete sump 4 ft. square, in which near the top is an inclined ½-in. round-hole screen to collect trash. The pump requires a new cover and impeller once in about 8 months.

The Dorr classifiers are equipped with four water nozzles of ⅜-in. diameter just above the rake line at the overflow end; this is to prevent the caking of the limestone above the rakes and the choking of the machine. Classifiers are elevated 3½ in. per ft. and make 26 strokes per minute. The products of the classifiers are as follows:

DORR-CLASSIFIER OVERFLOW

Screen Size	Size, Millimeters	Solids: Per Cent. Weight	Solids: Cumulative Per Cent. Weight	Zinc: Assay, Per Cent. Zinc	Zinc: Cumulative Assay, Per Cent.	Zinc: Per Cent. Total Zinc	Zinc: Cumulative Per Cent. Total Zinc
On 65 mesh	0.208	5.4	5.4	0.75	0.75	0.9	0.9
On 100 mesh	0.147	11.0	16.4	1.70	1.40	3.9	4.8
On 150 mesh	0.104	11.0	27.4	3.80	2.36	8.7	13.5
On 200 mesh	0.076	17.3	44.7	5.65	3.63	20.3	33.8
Through 200 mesh	0.076	55.3	100.0	5.75	4.80	66.2	100.0
Total		100.0	100.0	4.80	4.80	100.0	100.0
Original sample				4.80			

DORR-CLASSIFIER RETURNS

Screen Size	Size, Millimeters	Solids: Per Cent. Weight	Solids: Cumulative Per Cent. Weight	Zinc: Assay, Per Cent. Zinc	Zinc: Cumulative Assay, Per Cent	Zinc: Per Cent. Total Zinc	Zinc: Cumulative Per Cent. Total Zinc
On 20 mesh	0.832	3.3	3.3	0.90	0.90	0.3	0.3
On 35 mesh	0.416	16.3	19.6	3.15	2.80	5.4	5.7
On 65 mesh	0.208	43.4	63.0	6.80	5.50	30.8	36.5
On 100 mesh	0.147	18.7	81.7	16.00	7.88	30.8	67.3
On 150 mesh	0.104	7.5	89.2	23.00	9.17	18.0	85.3
On 200 mesh	0.076	4.8	94.0	18.50	9.65	9.2	94.5
Through 200 mesh	0.076	6.0	100.0	8.90	9.59	5.5	100.0
Total		100.0	100.0	9.59	9.59	100.0	100.0
Original sample				9.20			

All the grinding mills were originally pebble mills but four of them have been converted to ball and rod mills. Pebble grinding has proved very cheap, but on account of grinding coarser material and lack of capacity, the mills were converted to ball mills. Size D Danish flint pebbles and 4-in. quartzite cubes from Iowa are used in one mill with Forbes manganese-steel lining of the design shown in Fig. 10.

Local hard iron lining is used in all other mills with both steel and iron balls of various makes. The rod-mill practice, as an operation, is more expensive than ball-mill grinding but produces a more granular product.

Data on Grinding Medium, Fine-grinding Plant

Mill	No. 1				No. 1				No. 2			
Mill	5 ft. 6 in. by 10 ft. P & M				5 ft. 6 in. by 10 ft. P & M				7 by 10 ft. P & M			
Drive	Herringbone direct				Herringbone direct				Spur-gear belt drive			
Grinding Medium	2½-in. iron balls				2-in. and 3-in. iron cubes				3-in. iron rods			
Speed of Mill	23 r. p. m.				23 r. p. m.				12 r. p. m.			
	Feed		Overflow		Feed		Overflow		Feed		Overflow	
	Per Cent.	Cumulative, Per Cent.	Per Cent.	Cumulative, Per Cent.	Per Cent.	Cumulative, Per Cent.	Per Cent.	Cumulative, Per Cent.	Per Cent.	Cumulative, Per Cent.	Per Cent.	Cumulative, Per Cent.
On 3 mesh	0.8	0.8			3.1	3.1			0.4	0.4		
On 6 mesh	5.8	6.6			8.9	12.0			6.5	6.9		
On 10 mesh	29.9	36.5			32.9	44.9			33.1	40.0		
On 20 mesh	24.7	61.2			21.5	66.4			23.6	63.6		
On 35 mesh	17.7	78.9			15.3	81.7			15.9	79.5		
On 65 mesh	11.0	89.9	0.2	0.2	9.8	91.5	2.2	2.2	10.5	90.0	0.4	0.4
On 100 mesh	5.3	95.2	3.0	3.2	4.3	95.8	7.3	9.5	5.4	95.4	8.1	8.5
On 150 mesh	2.5	97.7	12.8	16.0	1.9	97.7	10.8	20.3	2.7	98.1	21.7	30.2
On 200 mesh	0.9	98.6	15.5	31.5	1.2	98.9	17.6	37.9	0.6	98.7	20.3	50.5
Through 200 mesh	1.4	100.0	68.5	100.0	1.1	100.0	62.1	100.0	1.3	100.0	49.5	100.0
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Solids in feed, per cent	60.0		15.0		63.0		15.4		70.0		15.6	
Dilution	1.0 to 1.5		5.68 to 1		1.0 to 1.71		5.51 to 1		1.0 to 2.33		5.46 to 1	
Average size of material, millimeters	1.563		0.088		1.864		0.097		1.6		0.1	
Ratio of reduction	17.96 to 1				19.2 to 1				16.0 to 1			
Dry tons in 24 hr	166		166		167		167		216		216	
Dry tons in 1 hr	7		7		7		7		9		9	

Total hours of test	1,330	1,978	1,428
Total tons of material finished	9,310	13,346	12,852
Grinding medium consumption, pounds	8,700	16,158	14,000
Grinding medium consumption per ton finished, pounds	0.934	1.21	1.1
Average number kilowatts per ton of feed	10.1	11.96	10.65
Average number kilowatts per 24 hr.	1,690	1,997	2,300
Tons of −65-mesh produced	8,392	12,115	11,538
Tons of −65-mesh in 24 hr.	151	147	194
Medium consumption per ton −65-mesh produced, pounds	1.11	1.33	1.21
Average number of kilowatts per ton − 65-mesh produced	11.2	13.6	11.8
Tons of −100-mesh produced	8,246	11,950	11,781
Tons of −100-mesh in 24 hr.	149	145	198
Medium consumption per ton −100-mesh produced, pounds	1.13	1.35	1.19
Average number of kilowatts per ton −100-mesh produced	11.3	13.7	11.6
Average numbers of kilowatt for mill	70.1	84.1	95.5
Average number of horsepower for mill	94.0	112.7	128
Period of test	6-12-23 to 9-1-23	9-3-23 to 12-15-23	6-4-23 to 8-21-23
Cost grinding medium per ton-65-mesh material produced	$0.0394	$0.0520	$0.0349
Charge in mill, pounds	20,000	20,000	50,000
Cost of steel per pound, in cents	3.55	3.90	2.88
Actual cost grinding medium per ton finished, in cents	3.736	4.719	5.500
Cost per ton steel and power based on 4 cents for rods and balls and 3.9 cents for cubes, in cents	11.57	14.099	13.764

Lining of the 5½ by 22 ft. mills weighs 33,101 lb. and lasts one year at a cost of 1.5 cents per ton of finished material.

The test results of two mills showing average practice follow. The use of iron cubes has been discontinued. It has been found that in addi-

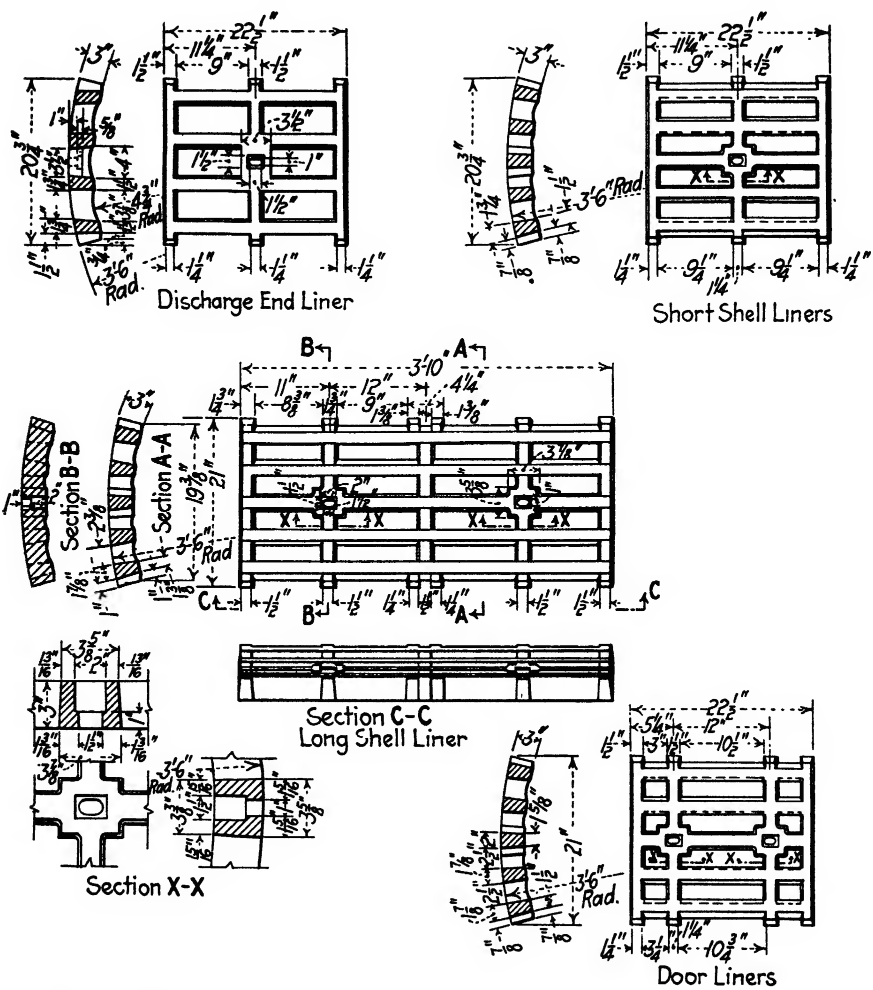


FIG. 10.—FIVE-BAR PATTERN, FORBES TUBE-MILL LINING FOR FLINT PEBBLES.

tion to rod consumption shown in the test, the flat and small rods discarded amount to 0.70 lb. per ton, which makes a total rod consumption between 1.70 and 2.00 lb. per ton finished of material. The test results submitted were obtained while producing a finer product than is now made.

The overflow from the Dorr classifiers, together with the dewatering overflows from the jig department, are thickened in Dorr thickeners to 4

to 1 dilution and pumped to the flotation plant. The Dorr overflow is clear water for re-use in the mill circuit.

DATA ON WILFLEY SLIME PUMP FOR ELEVATING FEED TO FLOTATION MILL

Size of pump	No. 4
Revolutions per minute	1200
Drive	10-in. belt
Gallons per minute	325
Dilution	4 to 1
Dry tons per hour	30–35
Discharge lift, feet	75
Pressure at pump, pounds	35–40
Size of pipe, inches	6
Length of pipe, feet	300
Intake head above pump shaft, inches	30
Size of pipe, inches	6
Length of pipe, feet	6
Mesh	20 per cent. + 100
Specific gravity of solids	3.00
Character	90 per cent. dolomite 10 per cent. sphalerite
Efficiency	44.4 per cent.

FLOTATION DEPARTMENT

The flotation feed, averaging 3.9 per cent. zinc, thickened to 50 per cent. solids, is given a preliminary mixing with reagents in a three-

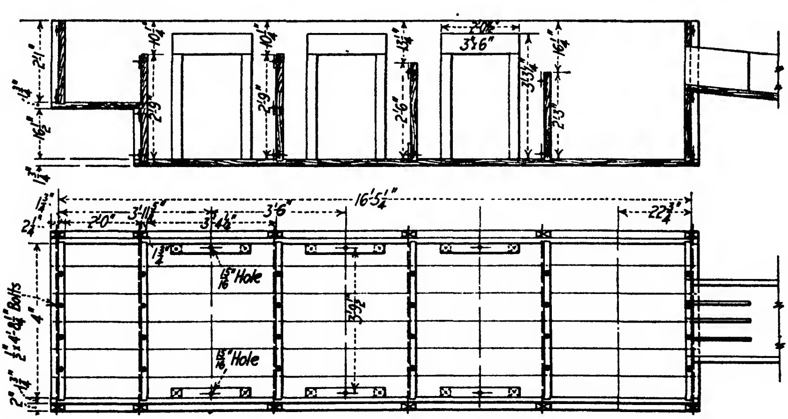


FIG. 11.—PRELIMINARY MIXER FOR REAGENTS.

compartment chamber and floated in seven Janney rougher cells in series arranged for gravity flow. The froth of the first two cells is cleaned in a two-cell series Janney cleaner and froth from the last five rougher cells, together with cleaner tails, comprises the return middling.

The original feed to the flotation mill is thickened to 50 per cent. solids in four 30-ft. Dorr thickeners discharg'ng through 4-in. lines, which are

controlled by stopcocks placed close to the tank bottom. The feed is given a preliminary agitation in a three-series compartment chamber, shown in Fig. 11. Each compartment is agitated by a standard vertical Janney motor equipped with one 13-in. diameter blade. The function of this mixer is to incorporate thoroughly the reagents with the pulp. The construction is entirely of wood. Reagents used are General Naval Stores No. 5 steam-distilled pine oil, commercial copper sulfate, and thiocarbanilid. All the copper sulfate and thiocarbanilid are added at the entrance to the mixer together with 70 per cent. of the pine oil used,

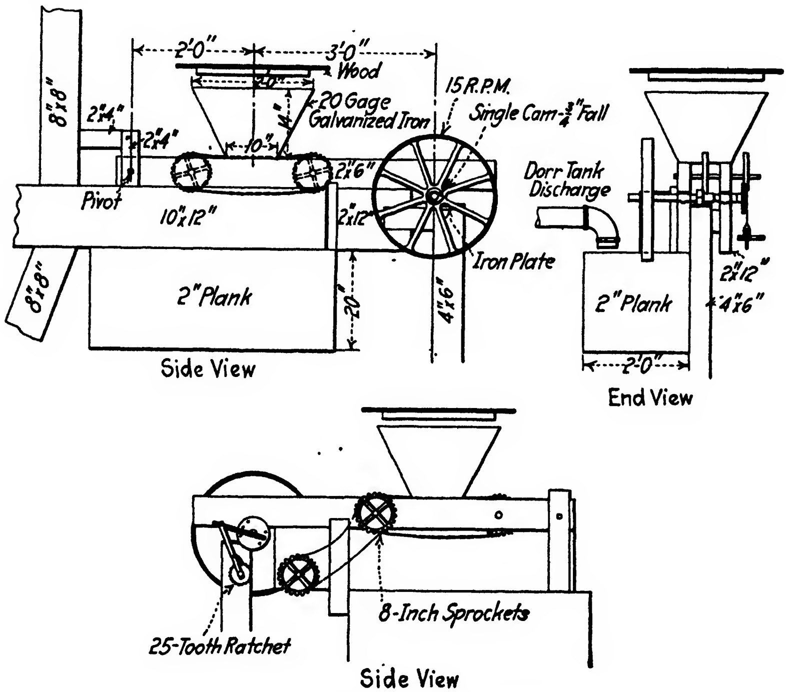


FIG. 12.—THIOCARBANILID FEEDER.

one-half of the balance being added to No. 3 rougher cell, and the rest to No. 5 rougher cell. All return middlings, consisting of cleaner tails and the overflow of the last five rougher cells, are returned to the middle chamber of the preliminary mixer. The thiocarbanilid is fed at the rate of 25 gm. per min. with the feeding arrangement shown in Fig. 12.

The cam on the driving shaft lifts and drops the thiocarbanilid hopper ½ in., thus keeping the reagent from arching over on the hopper. The small sprocket chain driven by the Reeves variable-speed control feeds the reagent in very small amounts with perfect regularity.

Copper sulfate is made into a 20 per cent. water solution in lead tanks and fed through a rubber hose and petcock by gravity. Pine oil is fed

from the main storage tank by gravity through a petcock. Return middlings are fed by gravity through an 8-in. pipe from a circular wooden surge tank, the discharge being regulated by a stopcock.

Liners and impellers made by Kellar Foundry Co. of Knoxville, are used. Impellers are spaced 12½ in. between blades with a 13-in. diameter blade on the bottom. Liners last 18 months and impeller blades 10 months. Spitzkastens on the cleaners are of the type shown in Fig. 13; those of the seven roughers are of the same construction but only 24 in. wide. The first two roughers are equipped with double spitzkastens, while all other cells have but the single spitzkasten. Skimmers are used

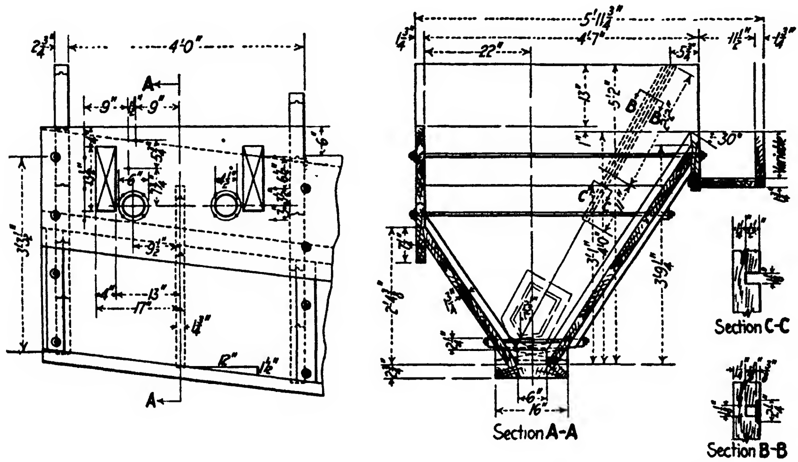


FIG. 13.—DETAIL OF SPITZKASTEN FOR JANNEY CLEANER CELL.

on the two double roughers and on the cleaners, as the froth on these cells forms a dense compact blanket mass.

The tailing, averaging 0.09 per cent. zinc with 1.70 to 1 dilution, is pumped through 1500 ft. of 6-in. pipe to the limestone plant. Concentrates, averaging 60.50 per cent. zinc and 40 per cent solids, are pumped through 450 ft. of 4-in. line to the concentrate-drying department.

FLOTATION PHYSICAL DATA, JANUARY–MARCH, 1924

Dry feed, tons	58,634
Assay per cent. zinc feed	3.90
Assay per cent. zinc tails	0.09
Assay per cent. zinc concentrates	60.64
Pine oil per ton feed, pounds	0.293
Copper sulfate per ton feed, pounds	0.313
Thiocarbanilid per ton feed, pounds	0.114
Extraction, per cent	97.80
Electric power, kilowatt-hour per ton feed	2.98
Gallons fresh water per minute	200

The two principal features in the control of the operation of the cells are the necessity of a heavy dilution on the new feed and the use of plenty of fresh water to dilute the cleaner feed. All the fresh water used in the plant is employed for diluting the cleaner feed. Mine water is used for this purpose in order to insure a uniform clear water supply, as occasionally the main mill-water supply is contaminated because of faulty settling in the mill Dorr thickeners and to heavy rains, which are frequent. No return water of any description is used in the flotation department. A general distribution of the values throughout the flotation cells, with dilutions, is as follows:

Product	Assay Per Cent. Zinc	Dilution, Weight Water to Solids
New feed	3.90	4 to 1
New feed dewatered	3.90	1 to 1
Machine feed	4.15	2.44 to 1
Plant tails	0.09	1.70 to 1
Plant concentrates (cleaner froth)	60.60	1 to 1
Cleaner feed (before adding dilution water)	48.00	3.82 to 1
Cleaner tails	22.80	15.1 to 1
Total plant middling	7.50	7.32 to 1
No. 3 rougher cell froth overflow	8.00	3.62 to 1
No. 4 rougher cell froth overflow	4.45	5.01 to 1
No. 5 rougher cell froth overflow	2.20	5.01 to 1
No. 6 rougher cell froth overflow	1.40	5.06 to 1
No. 7 rougher cell froth overflow	0.70	5.07 to 1

SCREEN TESTS OF FLOTATION PRODUCTS

Screen Size	Feed		Concentrates	
	Per Cent. Total Solids	Cumulative, Per Cent. Solids	Per Cent. Total Solids	Cumulative, Per Cent. Solids
On 65 mesh	8.0	8.0	1.4	1.4
On 100 mesh	12.8	20.8	6.5	7.9
On 150 mesh	14.0	34.8	12.9	20.8
On 200 mesh	16.0	50.8	16.9	37.7
Through 200 mesh	49.2	100.0	62.3	100.0
Total	100.0	100.0	100.0	100.0

FLOTATION TAILS

Screen Size	Solids: Per Cent. Total Solids	Solids: Cumulative, Per Cent. Solids	Zinc: Assay, Per Cent. Zinc	Zinc: Cumulative Assay, Per Cent. Zinc	Zinc: Per Cent. Total Zinc	Zinc: Cumulative Total Zinc Per Cent.
On 65 mesh	8.8	8.8	0.08	0.08	7.5	7.5
On 100 mesh	13.3	22.1	0.07	0.08	9.9	17.4
On 150 mesh	14.0	36.0	0.07	0.07	10.4	27.8
On 200 mesh	12.9	48.9	0.09	0.08	12.3	40.1
Through 200 mesh	51.0	100.0	0.11	0.09	59.9	100.0
Total	100.0	100.0	0.09	0.09	100.0	100.0

OPERATING DATA OF FLOTATION WILFLEY PUMPS

	CONCENTRATES	TAILS	MIDDLING
Size of pump	No. 4	No. 4	No. 4
Revolutions per minute	1200	1200	960
Drive	8-in. belt	8-in. belt	8-in. belt
Gallons per minute	20	250	200
Dry tons per hour	3	30	8
Discharge lift, feet	5	15	45
Pressure at pump, pounds	5	15	20
Size of pipe, inches	4	6	4
Length of pipe, feet	450	1500	80
Intake head above pump shaft, inches	18	36	36
Size of pipe, inches	4	6	4
Length of pipe, feet	1	8	4
Mesh	5 per cent. + 100	22 per cent. + 100	10 per cent. + 100
Character	Sphalerite	Dolomite	10 per cent. sphalerite 90 per cent. dolomite

FLOTATION OPERATING COSTS

ITEM	CENTS PER TON DRY FEED
Labor (operators)	2.18
Supervision (foreman)	0.80
Supplies (oil, waste, heat, etc.)	0.23
Reagents	6.82
Repairs and renewals	0.68
Power	2.53
Assaying laboratory	3.66
Total (without royalties)	16.90

This cost includes operation of Dorr thickeners and middling and concentrate pumps but not the tailing pump. The power cost includes 0.15 cents per ton charged for air used in operating automatic samplers.

MILL-WATER SUPPLY

Water for the mill supply is pumped from the creek mill race, a distance of 600 ft., with a 2000-gal. Prescott pump. At the mill Dorr thickeners, a 2500-gal. Prescott pump takes the overflow from the tanks.

Both these pumps discharge into a steel standpipe. Gallons pumped per minute, 4500; tons of water per ton ore, 11. Fresh water used in flotation department is from No. 1 mine.

Concentrate Drying and Loading

Jig concentrates are crushed through 10 mesh mixed with flotation concentrates, dried to 0.30 per cent. water and shipped in bulk in box cars, to the plant of the American Zinc Oxide Co. at Columbus, Ohio, where it is converted into high-grade zinc oxide.

Jig Concentrates

Jig concentrates, comprising about 30 per cent. of the total production, are trammed to the drying department, screened in a 4 by 8 ft. trommel through a ⅛-in. round-hole screen operating in closed circuit with a set of 12 by 20-in. rolls. The undersize of the screen is conveyed by a 12-in. screw conveyor to a 75-ton wood storage bin above the dryer, to which it is fed with an oscillating tray feeder. The crushed jig concentrate joins the filter cake at the feed end of the dryer. The moisture in the concentrates (2 to 4 per cent.) is just enough to make inefficient screening. This is overcome by using a hot-air blowpipe along the face of the trommel, the air being heated by a coil in the discharge end of the dryer.

Flotation Concentrates

These are thickened in a 30-ft. diameter by 20-ft. deep Dorr thickener to 50 to 60 per cent. solids and filtered on a 5 ft. 4 in. diameter by 8 ft. Oliver continuous filter, using 24-in. vacuum and 8 to 12 lb. air for blowing.

Data on Oliver Flotation-concentrate Filter

Solids filtered per 24 hr., tons	50
Filtrate, gallons per minute	8
Capacity per square foot filter area, pounds	1096
Cake, inch	½–⅝
Moisture in cake, per cent	8–9
Density pulp to filter, per cent. solids	50–60
Speed of drum, minutes per revolution	6
Pulp level below drum center, inches	24
Submergence of drum, per cent	25
Vacuum pump	Oliver Type M.O. Belt-driven 14-in. diameter by 8-in. stroke
Vacuum pump, revolutions per minute	188
Vacuum pump, displacement, cubic feet per minute	251
Vacuum maintained, inches	20–24
Displacement per square foot of cover, cubic feet	1.9
Solution pump	2-in. American
Solution pump	9-in. runner
Solution pump, revolutions per minute	1200

Filter blow, pounds of air	12
Type of agitator	Oscillating rake
Filter cover	Oliver 3–0 canvas
Life of cover, weeks	10
Wire used	No. 14 galvanized steel
Wire spacing	16 wraps per foot.
Cleaning of cover	Scrubbed and washed every 6 days
Screen tests of feed	See under flotation plant

The filter cake is discharged by gravity onto a 12 by 28 ft. Lowden dryer fired with 28 gravity fuel oil. With oil firing, there are practically no repairs to the furnace or dryer, the plates on the dryer top lasting indefinitely. A Bristol recording pyrometer is used for operators' control of the temperature.

The dryer load averages 75 to 80 tons dry concentrates per day with an oil consumption of 5½ gal. per ton of concentrates dried.

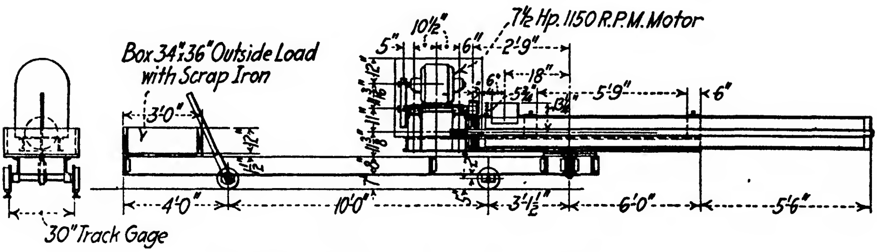


Fig. 14.—Concentrates car loader used.

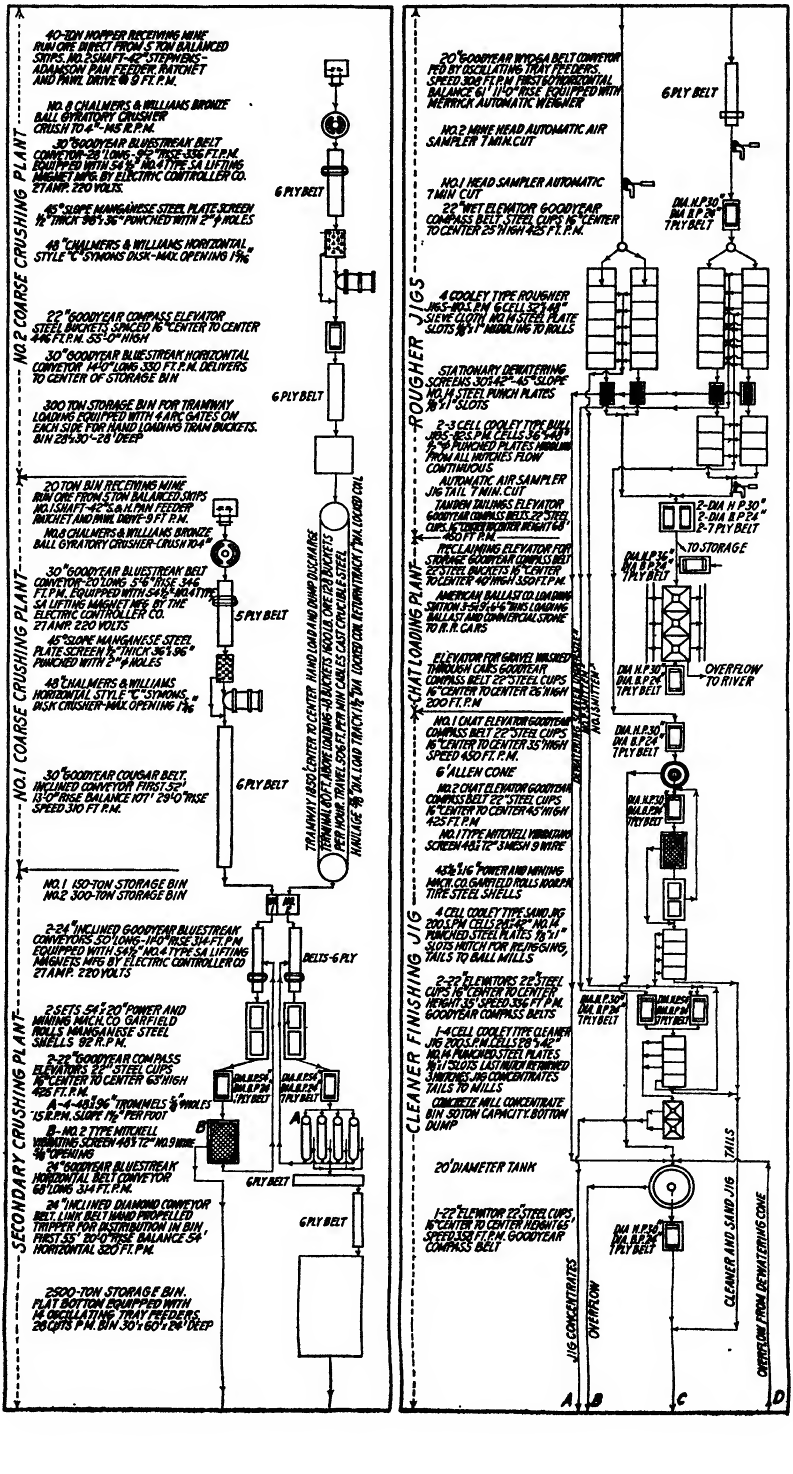
To prevent dusting at the dryer discharge, a screw conveyor seal is used; this is so regulated as to keep a bank of material over the opening into the conveyor, thus preventing any air escaping from the conveyor. A Link Belt all-iron elevator raises the dried concentrate to a 20 by 20 ft. circular steel bin from which it is loaded by one man, using the type of loader shown in Fig. 14. This loader has a capacity of 30 tons per hour. Very little dust loss is incurred, the cars being loaded in the open.

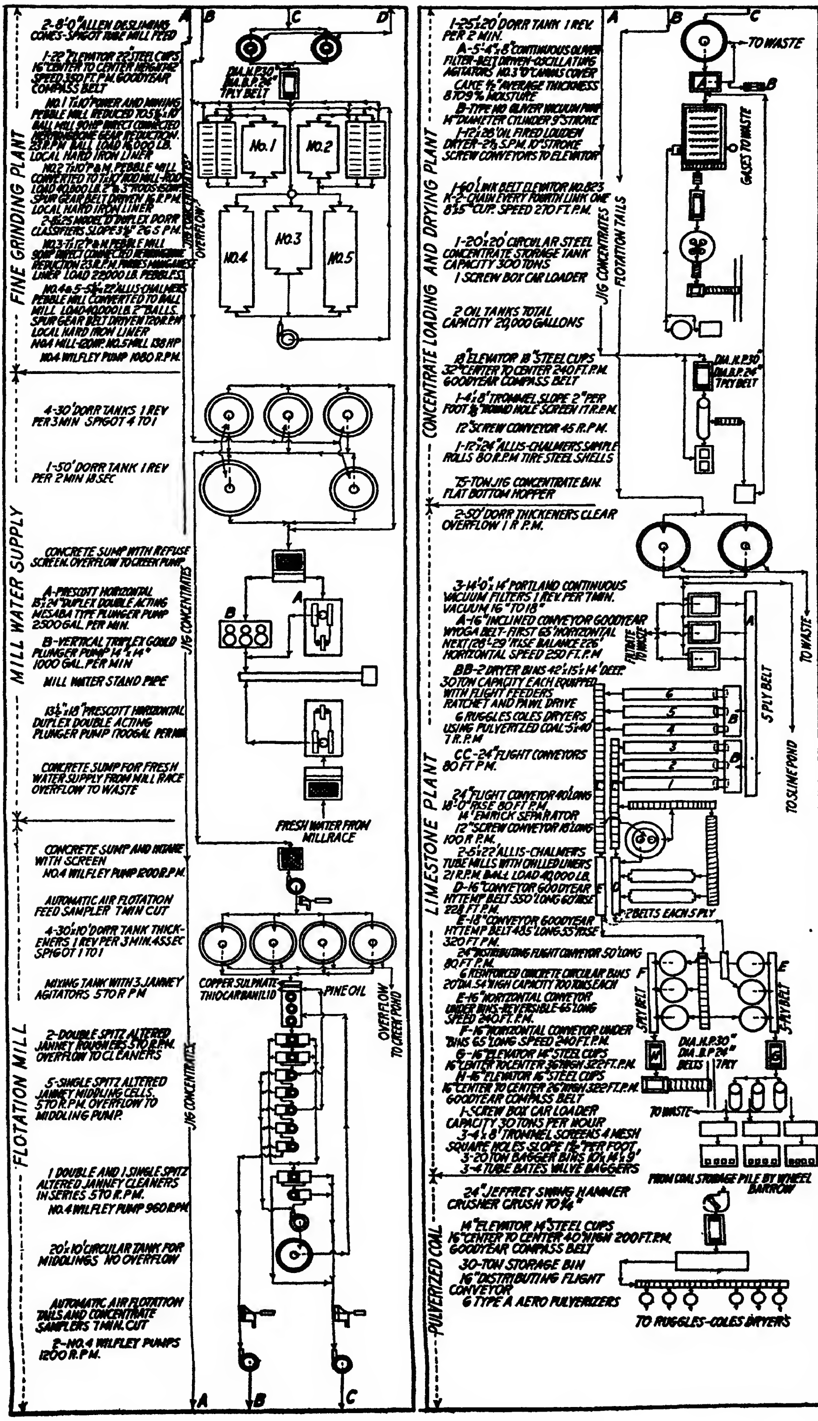
Concentrate Handling Costs, in Cents per Ton

Item	Handled	Total Shipped
Tramming, crushing and screening jig concentrates	41.48	10.50
Pumping and thickening flotation concentrates	6.52	4.70
Filtering flotation concentrates	23.71	17.70
Drying and elevating total concentrates	62.17	62.17
Loading	13.93	13.93
Total handling cost	109.00	109.00

Mill Sampling

Different sampling devices used throughout the mill are shown in Fig. 15. Car samples are obtained with the gun sampler and jig concentrates are sampled as trammed from the jigs, with the pipe sampler. All


NO. 2 COARSE CRUSHING PLANT
40-TON HOPPER RECEIVING MINE RUN ORE DIRECT FROM 5 TON BALANCED SKIPS. NO. 2 SHAFT-42" STEPHENS-ADAMSON PAN FEEDER. RATCHET AND PAWL DRIVE @ 9 FT. P.M.
NO. 8 CHALMERS & WILLIAMS BRONZE BALL GYRATORY CRUSHER CRUSH TO 4"-145 R.P.M.
30" GOODYEAR BLUESTREAK BELT CONVEYOR-28' LONG-9'2" RISE-336 FT. P.M. EQUIPPED WITH 54½" NO. 4 TYPE SA LIFTING MAGNET MFG. BY ELECTRIC CONTROLLER CO. 27 AMP. 220 VOLTS.
45° SLOPE MANGANESE STEEL PLATE SCREEN ½" THICK 96"x36" PUNCHED WITH 2" φ HOLES
48" CHALMERS & WILLIAMS HORIZONTAL STYLE "C" SYMONS DISK-MAX. OPENING 1 3/16"
22" GOODYEAR COMPASS ELEVATOR STEEL BUCKETS SPACED 16" CENTER TO CENTER 446 FT. P.M. 55'-0" HIGH
30" GOODYEAR BLUESTREAK HORIZONTAL CONVEYOR 14'-0" LONG 330 FT. P.M. DELIVERS TO CENTER OF STORAGE BIN
300 TON STORAGE BIN FOR TRAMWAY LOADING EQUIPPED WITH 4 ARC GATES ON EACH SIDE FOR HAND LOADING TRAM BUCKETS. BIN 28'x30'-28' DEEP
6 PLY BELT
6 PLY BELT
NO. 1 COARSE CRUSHING PLANT
20 TON BIN RECEIVING MINE RUN ORE FROM 5 TON BALANCED SKIPS NO. 1 SHAFT-42" S.&H. PAN FEEDER RATCHET AND PAWL DRIVE-9 FT. P.M.
NO. 8 CHALMERS & WILLIAMS BRONZE BALL GYRATORY CRUSHER-CRUSH TO 4"
30" GOODYEAR BLUESTREAK BELT CONVEYOR-20' LONG 5'-6" RISE 346 FT. P.M. EQUIPPED WITH 54½" NO. 4 TYPE SA LIFTING MAGNET MFG. BY THE ELECTRIC CONTROLLER CO. 27 AMP. 220 VOLTS
45° SLOPE MANGANESE STEEL PLATE SCREEN ½" THICK 36"x96" PUNCHED WITH 2" φ HOLES
48" CHALMERS & WILLIAMS HORIZONTAL STYLE "C" SYMONS DISK CRUSHER-MAX. OPENING 1 3/16"
30" GOODYEAR COUGAR BELT. INCLINED CONVEYOR FIRST 52' 13'-0" RISE BALANCE 107' 29'-0" RISE SPEED 310 FT. P.M.
5 PLY BELT
6 PLY BELT
TRAMWAY 1850' CENTER TO CENTER. HAND LOAD AND DUMP DISCHARGE TERMINAL 60 FT. ABOVE LOADING-40 BUCKETS 1600 LB. ORE 120 BUCKETS PER HOUR. TRAVEL 506 FT. PER MIN. CABLES CAST CRUCIBLE STEEL HAULAGE 5/8" DIA. LOAD TRACK 1½" DIA. LOCKED COIL. RETURN TRACK 1" DIA. LOCKED COIL
SECONDARY CRUSHING PLANT
NO. 1 150-TON STORAGE BIN
NO. 2 300-TON STORAGE BIN
2-24" INCLINED GOODYEAR BLUESTREAK CONVEYORS 50' LONG-11'-0" RISE 314 FT. P.M. EQUIPPED WITH 54½" NO. 4 TYPE SA LIFTING MAGNETS MFG. BY ELECTRIC CONTROLLER CO. 27 AMP. 220 VOLTS
2 SETS 54"x20" POWER AND MINING MACH. CO. GARFIELD ROLLS MANGANESE STEEL SHELLS 92 R.P.M.
2-22" GOODYEAR COMPASS ELEVATORS 22" STEEL CUPS 16" CENTER TO CENTER 63' HIGH 425 FT. P.M.
A-4-48"x96" TROMMELS 5/8" φ HOLES 15 R.P.M. SLOPE 1½" PER FOOT
B-NO. 2 TYPE MITCHELL VIBRATING SCREEN 48"x72" NO. 9 WIRE 3/8" OPENING
24" GOODYEAR BLUESTREAK HORIZONTAL BELT CONVEYOR 68' LONG 314 FT. P.M.
24" INCLINED DIAMOND CONVEYOR BELT. LINK BELT HAND PROPELLED TRIPPER FOR DISTRIBUTION IN BIN. FIRST 55' 20'-0" RISE BALANCE 54' HORIZONTAL 320 FT. P.M.
2500-TON STORAGE BIN. FLAT BOTTOM EQUIPPED WITH 14 OSCILLATING TRAY FEEDERS. 28 CU. FT. P.M. BIN 30'x60'x24' DEEP
BELTS-6 PLY
DIA. H.P. 54" DIA. B.P. 36" 7 PLY BELT
DIA. H.P. 54" DIA. B.P. 36" 7 PLY BELT
A
B
6 PLY BELT
6 PLY BELT
ROUGHER JIGS
20" GOODYEAR WYOGA BELT CONVEYOR FED BY OSCILLATING TRAY FEEDERS. SPEED 308 FT. P.M. FIRST 60' HORIZONTAL BALANCE 61' 11'-0" RISE EQUIPPED WITH MERRICK AUTOMATIC WEIGHER
NO. 2 MINE HEAD AUTOMATIC AIR SAMPLER 7 MIN. CUT
NO. 1 HEAD SAMPLER AUTOMATIC 7 MIN CUT
22" WET ELEVATOR GOODYEAR COMPASS BELT. STEEL CUPS 16" CENTER TO CENTER 25' HIGH 425 FT. P.M.
4 COOLEY TYPE ROUGHER JIGS-190 S.P.M. 6 CELL 32"x48" SIEVE CLOTH. NO. 14 STEEL PLATE SLOTS 3/8"x1" MIDDLING TO ROLLS
STATIONARY DEWATERING SCREENS 30"x42"-45° SLOPE NO. 14 STEEL PUNCH PLATES 3/8"x1" SLOTS
2-3 CELL COOLEY TYPE BULL JIGS-182 S.P.M. CELLS 36"x48" ½" φ PUNCHED PLATES MIDDLING FROM ALL HUTCHES FLOW CONTINUOUS
AUTOMATIC AIR SAMPLER JIG TAIL 7 MIN. CUT
TANDEM TAILINGS ELEVATOR GOODYEAR COMPASS BELTS 22" STEEL CUPS 16" CENTER TO CENTER HEIGHT 68' 480 FT. P.M.
6 PLY BELT
DIA. H.P. 30" DIA. B.P. 24" 7 PLY BELT
2-DIA. H.P. 30" 2-DIA. B.P. 24" 2-7 PLY BELT
CHAT LOADING PLANT
RECLAIMING ELEVATOR FOR STORAGE GOODYEAR COMPASS BELT 22" STEEL BUCKETS 16" CENTER TO CENTER 40' HIGH 350 FT. P.M.
AMERICAN BALLAST CO. LOADING STATION 3-5/8, 6-16 " BINS LOADING BALLAST AND COMMERCIAL STONE TO R.R. CARS
ELEVATOR FOR GRAVEL WASHED THROUGH CARS GOODYEAR COMPASS BELT 22" STEEL CUPS 16" CENTER TO CENTER 26' HIGH 200 FT. P.M.
TO STORAGE
DIA. H.P. 36" DIA. B.P. 24" 7 PLY BELT
DIA. H.P. 30" DIA. B.P. 24" 7 PLY BELT
OVERFLOW TO RIVER
CLEANER FINISHING JIG
NO. 1 CHAT ELEVATOR GOODYEAR COMPASS BELT 22" STEEL CUPS 16" CENTER TO CENTER 35' HIGH SPEED 450 FT. P.M.
6' ALLEN CONE
NO. 2 CHAT ELEVATOR GOODYEAR COMPASS BELT 22" STEEL CUPS 16" CENTER TO CENTER 45' HIGH 425 FT. P.M.
NO. 1 TYPE MITCHELL VIBRATING SCREEN 48"x72" 3 MESH 9 WIRE
43½"x16" POWER AND MINING MACH. CO. GARFIELD ROLLS 100 R.P.M. TIRE STEEL SHELLS
4 CELL COOLEY TYPE SAND JIG 200 S.P.M. CELLS 28"x42" NO. 14 PUNCHED STEEL PLATES 3/8"x1" SLOTS HUTCH FOR RE-JIGGING, TAILS TO BALL MILLS
2-22" ELEVATORS 22" STEEL CUPS 16" CENTER TO CENTER HEIGHT 35' SPEED 336 FT. P.M. GOODYEAR COMPASS BELTS
1-4 CELL COOLEY TYPE CLEANER JIG 200 S.P.M. CELLS 28"x42" NO. 14 PUNCHED STEEL PLATES 3/8"x1" SLOTS LAST HUTCH RETURNED 3 HUTCHES JIG CONCENTRATES TAILS TO MILLS
CONCRETE MILL CONCENTRATE BIN 50 TON CAPACITY. BOTTOM DUMP
20' DIAMETER TANK
1-22" ELEVATOR 22" STEEL CUPS 16" CENTER TO CENTER HEIGHT 65' SPEED 358 FT. P.M. GOODYEAR COMPASS BELT
DEWATERING SCREEN UNDERSIZE
NO. 1 SMITTEN
DIA. H.P. 30" DIA. B.P. 24" 7 PLY BELT
DIA. H.P. 30" DIA. B.P. 24" 7 PLY BELT
DIA. H.P. 30" DIA. B.P. 24" 7 PLY BELT
DIA. H.P. 30" DIA. B.P. 24" 7 PLY BELT
DIA. H.P. 30" DIA. B.P. 24" 7 PLY BELT
TAILS
JIG CONCENTRATES
OVERFLOW
CLEANER AND SAND JIG
OVERFLOW FROM DEWATERING CONE
A
B
C
D



FINE GRINDING PLANT
MILL WATER SUPPLY
FLOTATION MILL
CONCENTRATE LOADING AND DRYING PLANT
LIMESTONE PLANT
PULVERIZED COAL
2-8'-0" ALLEN DESLIMING CONES-SPIGOT TUBE MILL FEED
No. 1
No. 2
No. 3
No. 4
No. 5
4-30' DORR TANKS 1 REV PER 3 MIN SPIGOT 4 TO 1
1-50' DORR TANK 1 REV PER 2 MIN 18 SEC
CONCRETE SUMP WITH REFUSE SCREEN. OVERFLOW TO GREEN POND
MILL WATER STAND PIPE
CONCRETE SUMP FOR FRESH WATER SUPPLY FROM MILL RACE OVERFLOW TO WASTE
FRESH WATER FROM MILLRACE
CONCRETE SUMP AND INTAKE WITH SCREEN
NO.4 WILFLEY PUMP 1200 R.P.M.
AUTOMATIC AIR FLOTATION FEED SAMPLER 7 MIN CUT
MIXING TANK WITH 3 JANNEY AGITATORS 570 R.P.M.
COPPER SULPHATE THIOCARBANILID
PINE OIL
OVERFLOW TO GREEN POND
JIG CONCENTRATES
20'x10' CIRCULAR TANK FOR MIDDLINGS NO OVERFLOW
2-NO.4 WILFLEY PUMPS 1200 R.P.M.
TO WASTE
GASES TO WASTE
JIG CONCENTRATES
FLOTATION TAILS
2 OIL TANKS TOTAL CAPACITY 20,000 GALLONS
2-50' DORR THICKENERS CLEAR OVERFLOW 1 R.P.M.
FILTRATE TO WASTE
5 PLY BELT
TO SLIME POND
2 BELTS EACH 5 PLY
5 PLY BELT
FROM COAL STORAGE PILE BY WHEEL BARROW
24" JEFFREY SWING HAMMER CRUSHER CRUSH TO 1/4"
30-TON STORAGE BIN
6 TYPE A AERO PULVERIZERS
TO RUGGLES-COLES DRYERS
A
B
C
D

wet sampling is done with the air actuated device using cutters. These samples are taken once in 7 min., one air valve operating all samplers in any one building. For sampling the dry mill heads, the same system is used except that the cutter is suspended on rollers instead of being pivoted. All mill samples are assayed every 8-hr. shift and results are posted in the mill.

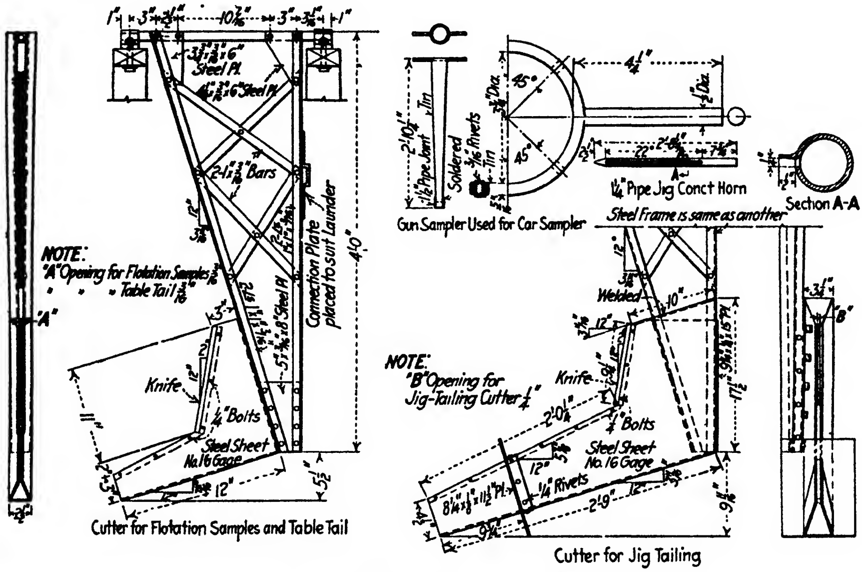


Fig. 15.—Sampling devices.

Mill Power Distribution

Department	Kilowatt-hours per ton Handled	Kilowatt-hours per ton Milled
Aerial tramway	0.12	0.07
No. 1 coarse-crushing plant	0.89	0.35
No. 2 coarse-crushing plant	0.99	0.60
Jigging department	1.27	1.27
Fine-crushing department	1.86	1.86
Grinding	10.71	3.53
Classifying and thickening	2.36	0.78
Elevating jig tails	0.46	0.29
Water supply		1.26
Pumping feed to flotation	0.46	0.29
Total wet mill		10.30
Flotation*	3.17	1.04
Total milling		11.34
Concentrate drying*	20.0	0.55
Grand total*		11.89

* Includes all air used in sampling and other requirements in each department.

Precipitation Efficiency of Zinc Dust in Cyanide Process

By Robert Lepsoe, Bergen, Norway

(New York Meeting, February, 1925)

It is generally realized that in cyaniding the precipitation efficiency of zinc dust is due to the fine division or extended surface of its metallic particles; but frequently it is thought that the presence of other metals, say 2 to 3 per cent. lead, is advantageous, causing more complete precipitation. The results of testing about fifty brands of commercial zinc dust have led to the conclusion that there is a distinct relation of precipitation efficiency to fineness and that the effect generally can be estimated by examining the size of metallic particles. The presence of lead was not found to be of any importance.

Specifications

Generally the term "97 per cent. to pass a 350-mesh screen, 95 to 97 per cent. uncombined metallic zinc" is used by the leading European exporters. Among the many methods of determination of metallic zinc, I have found the iodine test (iodine in potassium iodide) very satisfactory and rapid. It has been controlled by the other methods, samples of the same product having been sent to three different analysts:

Iodine method	98.11 per cent. metallic zinc,
Volumetric method	97.63 per cent. metallic zinc, Ledoux Co., New York
Bichromate method	98.16 per cent. metallic zinc, Watson Gray, Liverpool, England
Bichromate method	98.20 per cent. metallic zinc, Norway Inst. of Tech., Trondhjem

Determination of Precipitation Efficiency

The method devised by W. J. Sharwood[1] was used. The method proved to be satisfactory, the tests being merely for the comparison of different samples, hence the personal factor in manipulation was eliminated. As nearly all tests showed more zinc in solution than was accounted for by the silver precipitated, the term "dissolved zinc" was introduced—it means zinc dissolved by the action of cyanide and oxygen:

$$Zn + 4KCN + H_2O + O = K_2Zn(CN)_4 + 2KOH;$$

or more probably, resolution of its equivalent precipitated silver, as tests stirred two hours showed more "dissolved zinc" than those stirred

[1] Cyanide Precipitants—A collection of articles. *Eng. & Min. Jnl.* (1914).

TABLE 1

Sample	Metallic Zinc, Per Cent.	Lead, Per Cent.	Iron, Per Cent.	+350 Mesh, Per Cent.	Per Cent. Prec. Eff.	Prec. Eff. Based on Metallic Zinc Content, Per Cent.	Metallic Zinc Left in Precip. Based on Metallic Zinc, Per Cent.	Dissolved Zinc Based on Metallic Zinc, Per Cent.	Microscopic Examination
1	96.0	0.10	0.09	1	31	32.0	68.0	0.0	Mostly 0.008 and 0.01; very bright, very few 0.004
2	94.8	n. d.	n. d.	3	29	30.5	58.0	11.0	
3	94.3	0.19	0.09	3	38	40.4	53.0	6.0	
4	95.0	1.24	0.015	3	29	31.0	64.0	5.0	Considerable 0.003, but mostly coarse, crystalline aggregates
5	98.0	1.02	0.01	30[a]	11	11.2	89.8	0	Crystalline, very coarse, corresponding to about 0.03 and 0.07
6	98.6	0.06	0.01	5	41	41.5	45.6	13.0	
7	97.2	0.34	0.02	2	48	49.5	39.0	11.5	Mixture 0.002, 0.004, and 0.008; bright 0.004 and 0.008; bright
8a	97.9	0.21	0.09	0	42	42.5	55.0	2.5	
8b	97.9	0.21	0.09	0	47	48.0	51.0	1.0	Mostly 0.004, but considerable 0.008; bright[c] 0.004, very few 0.008 and 0.002; bright[c]
8c	97.9	0.21	0.09	0	51	52.0	43.0	5.0	
9	94.0	3.20	0.07	0.6	55	58.0	29.0	13.0	Mostly 0.004, but considerable 0.003; less bright
10	92.7	2.70	0.07	0.8	48	51.3	41.0	7.7	
11	92.1	0.34	0.05	4	46	49.6	41.0	9.4	
12	94.8	0.18	n. d.	1	57	60.5	32.8	6.7	0.002 and 0.004, very few 0.008 and 0.01, less bright
13	92.2	0.05	n. d.	1	49	53.4	45.0	1.6	
14	91.0	n. d.	n. d.	0	55	60.5	27.0	12.5	About two-thirds 0.003, one-third 0.0002; dark
15	89.0	0.236	0.027	3	53	59.6	28.0	12.4	0.003 and 0.0025; dark
16	79.0	2.37	0.04	2	24	31.0	68.4	0.6	Not uniform, 0.008; 0.004 but considerable 0.03 oxide
17	86.5	2.7	0.03	5	29	33.5			
18	89.0	0.2	n. d.	35[b]	6	6.8	93.0	0.0	Very coarse; black

[a] 100 per cent. — 200-mesh. [b] 35 per cent. — 200-mesh. [c] Samples 8^2 and 8^3, fractions made by elutriation in a rising stream of water. Sherwood: *loc. cit.* p. 7.

one hour. To determine "dissolved zinc" the silver precipitate was dissolved in nitric acid, silver titrated with thiocyanate, and solution titrated with ferrocyanide (after removing silver precipitate) giving the amount of intact metallic zinc left in the zinc dust silver precipitate. The difference between active plus intact zinc and total metallic zinc is "dissolved zinc."

Sources of Zinc Dust Tested

Samples 1 to 4 are American zinc dust; 6 to 8 are Norwegian, electrothermic fumed dust; 9 to 14 are from an electrothermic experimental plant; 15, origin is unknown, sample was furnished by Ste. Generale de Commerce & Exterieur, Paris; 16 is Belgian dust; 17, German; and 18, electrothermic blue powder (byproduct from electrothermic zinc smelting). Samples 4 and 5 were atomized, the other distilled.

Precipitation Efficiency as a Factor of Fineness

The microscopic examination showed that the distilled zinc dust consists of almost perfect spherules. The appearance is almost clean and metallic except in samples 16 and 17, where numerous particles of oxide are shown. The atomized dust (samples 4 and 5) has a coke-like surface and is very coarse; especially sample 5, which was made by a 100 lb. air pressure.

The number of spheres in a pound zinc dust, assuming the specific gravity as 7. is $\frac{0.1235}{d^3}$, hence

if the diameter is 1 mm., 1 lb. will contain 123,500 particles
if the diameter is 0.1 mm., 1 lb. will contain 1235 million particles
if the diameter is 0.01 mm., 1 lb. will contain 123,500 million particles
if the diameter is 0.003 mm., 1 lb. will contain 4600 billion particles

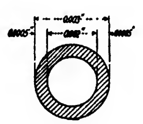


Fig. 1.

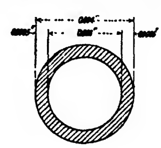


Fig. 2.

In sample 15, spherules of 0.003 mm. diameter were found to be predominant, hence the number of particles in 1 lb. (89 per cent. metallic zinc) is 4600 billion × 0.89 = 4100 billion. In the precipitate was left 28 per cent. of the dust's metallic zinc content, the diameter of remaining intact zinc spherules is then: 4100 billion $= \frac{0.1235}{d^3} \times 0.28$ and $d =$ 0.002 mm. The original spherule was 0.003 mm., hence the thickness of active surface is 0.0005 mm.

In sample 8,[3] the major particles were of 0.004 mm. diameter. The number of particles in 1 lb. is 2000 billion. In the precipitate was left 43 per cent. of the metallic zinc, then the diameter of the intact particle is 2000 billion $= \frac{0.1235}{d^3} \times 0.43$ and $d = 0.003$ mm. The thickness of active surface is 0.0005 mm. and so forth.

In the same manner, the efficiency of a zinc dust may be estimated on the basis of fineness as:

$$\frac{\frac{1}{6}\pi d^3 \div \frac{1}{6}\pi(d \div 0.001)^3}{\frac{1}{6}\pi d^3} \times 100 = \frac{d^3 \div (d \div 0.001)^3}{d^3} \times 100$$

The diameter examined being 0.002 mm., the efficiency is 88 per cent.

The diameter examined being 0.003 mm., the efficiency is 70.3 per cent.

The diameter examined being 0.004 mm., efficiency is 58.0 per cent.

The diameter examined being 0.008 mm., efficiency is 33.2 per cent.

The diameter examined being 0.01 mm., efficiency is 27.0 per cent.

The diameter examined being 0.03[a] mm., efficiency is 9.7 per cent.

The diameter examined being 0.07[b] mm., efficiency is 3.5 per cent.

To get a fair comparison between the found efficiencies and those from fineness estimated values, it is necessary to eliminate what is called "dissolved" zinc. This is possible by figuring the precipitation efficiency from the difference of metallic zinc left in precipitate; which is here called "true efficiency."

TABLE 2

Sample	True Efficiency, Per Cent.	Estimated Efficiency, Per Cent.
1	32	27–33.2
5	11	About 11
7	61	60
8a	45	45
8b	49	49
8c	57	56
9	71	63
12	68	72
14	73	75
15	72	73

From the foregoing data there is little doubt as to what role fineness is playing. The consumer frequently calls for high content of metallic zinc, but mostly he buys in accord with the efficiency obtained in practical running. The producer should, therefore, direct his attention to improving the fineness—under maintenance of the highest content of metallic zinc—until it becomes really fume.

[a] Corresponds to particles just passing through 350-mesh screen.
[b] Corresponds to particles just passing through 200-mesh screen.

DISCUSSION

G. M. Brown, New York, N. Y.—André Dorfmann of the McIntyre Porcupine Mine made a similar test, some years ago, relative to consumption of zinc and the results he obtained confirm the statements in this paper. In addition to the amount of zinc left in the precipitation presses, he determined the amount of zinc in the barren solution. As this solution was recirculated through the system, he also determined the amount of zinc precipitated from solution, in the ball-mill, tube-mill and agitators, before the solution was again returned to the precipitation presses.

Charles E. Locke, Cambridge, Mass.—The thing which struck me in looking through the table is that the maximum figure is about 60 per cent. efficiency, when based on the metallic zinc content, and the ordinary efficiency, if I interpret it correctly, ranges from a maximum of 57 per cent. with the finest dust down to 6 per cent. with some rather coarse samples of zinc dust.

Determination of Suspensoids by Alternating-current Precipitators

By Philip Drinker* and R. M. Thomson,* Boston, Mass.

(New York Meeting, February, 1925)

In the mining and metallurgical industries, numerous problems arise requiring determinations of solid and of liquid particles suspended in air. Frequently, these problems are of local interest and involve purely economic or operating difficulties; on the other hand, toxic effects from the inhalation or the ingestion of substances suspended in air may be a matter of concern. For checking up process improvements or for determining ventilation efficiencies in problems of this general nature, various methods have been proposed. Although simpler methods are often satisfactory, precipitation combines several desirable features that other methods lack. This paper is, therefore, devoted to a discussion of portable alternating-current precipitators applicable to the quantitative determination and microscopy of dusts, fumes, and smokes in air.

Small particles suspended in gases, such as air, are referred to in the literature as aerosols or suspensoids. Of these terms, suspensoids appears to be preferable as being more nearly in keeping with words in everyday use. In problems involving air pollution by small particles—by suspensoids—it is convenient to distinguish three broad classes based on the size, the degree of dispersion, and the method by which the particles become suspended in the air.

Dusts.—Particles or aggregates of particles, 150 to 1 micron in diameter, that are thrown into the air by mechanical agencies are termed dusts. Examples are silica; talc; cement; organic dusts such as hard rubber, starch, and cocoa; flocculated fume, and smoke products.

Fumes.—Particles, 0.2 to 1 micron in diameter, formed from chemical or physicochemical reactions are known as fumes. Examples are ammonium chloride, lead and mercury, zinc and magnesium oxides, fogs, and acid mists.

Smokes.—Particles, less than 0.3 micron in diameter, formed by incomplete combustion of carbonaceous and other substances are called smokes. Examples are the particles formed from burning tobacco, oil, tar, and gas.

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These classes resemble those originally suggested by Gibbs,[1] except that dusts cover a wider range of particle size and the size limitations for fumes and smokes overlap. In spite of obvious errors resulting from the inadequacies of classification, several features differentiating the three groups can be distinguished. Uniformity in the size of the particles and the tendency to flocculate or aggregate in air increase as the particles become smaller. Under still-air conditions and normal temperatures, dusts settle out with acceleration and do not diffuse. Fumes settle at rates approximating those predicted by Stokes' law and diffuse to some extent; while smokes diffuse, show Brownian movement, and settle so slowly that their settling rates, even in still air, may be ignored unless the particles become united into larger aggregates.

In establishing the principles and the practical operating details of his process, Cottrell was concerned, in his original work, with large installations. No attempt seems to have been made to develop small portable precipitators until Tolman, Reyerson, Brooks, and Smythe,[2] in 1919, described a suitable equipment. By means of high-tension current, rectified by a kenotron, particles were precipitated on a thin aluminum foil and the increase in weight of the foil determined. Somewhat later, Bill[3] published an account of dust determinations obtained with a small electric precipitator that differed from Tolman's in the use of a mechanical stick rectifier instead of a kenotron. At about the same time, Lamb, Wendt, and Wilson[4] described an electric fume or smoke mask in which a storage battery and an induction coil served as the source of high-tension current. These authors used glass tubes wrapped with metal foil for collecting electrodes, while the precipitating electrodes were made to bristle with sharp points protruding radially. Several of these tubes were placed together in a bundle with the connections for air flow and current in parallel. Although no rectifying device was utilized, the fact that this method, if glass tubes were used, could produce complete precipitation without complete rectification does not seem to have been considered. Strong[5] has obtained a patent for a small precipitator much like Lamb's, but in which only one tube is used. Lamb suggested using several tubes connected in parallel, although his quantitative data were obtained with but one tube.

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[1] W. E. Gibbs: The Industrial Treatment of Fumes and Dusty Gases. *Jnl.* Soc. Chem. Ind. (1922) **41**, 189T.

[2] R. C. Tolman, L. H. Reyerson, A. P. Brooks and H. D. Smyth: An Electrical Precipitator for Analyzing Smokes. *Jnl.* Am. Chem. Soc. (1919) **41**, 587.

[3] J. P. Bill: The Electrostatic Method of Dust Collection as Applied to the Sanitary Analysis of Air. *Jnl. Ind. Hyg.* (1919–20) **1**, 323.

[4] A. B. Lamb, G. L. Wendt and R. E. Wilson: A Portable Electric Filter for Smokes and Bacteria. *Trans.* Am. Electrochem. Soc. (1919) **35**, 357.

[5] W. W. Strong: U. S. Patent 1325124.

For studying the effects of covering the precipitating electrodes with glass tubes, Shibusawa and Niwa[6] used a small precipitator with a kenotron and a glass tube wrapped outside with metal foil. Like Tolman, they obtained the high-tension current from a transformer. By means of oscillograms, they showed the characteristics of the voltage and current curves obtained when the precipitating electrode was positive, negative, and when alternating current was used and no kenotron was in the circuit. No experimental precipitations were made, however, with alternating current.

Katz, Fieldner, and Longfellow[7] used a small precipitator, like Tolman's, but obtained unsatisfactory results. Drinker, Thomson, and Fitchet[8] used successfully a small portable precipitator having a glass tube, in which the current was supplied by a transformer, but in which no rectifier was used. Baumberger[9] and Salmang[10] both obtained satisfactory results with small rectified-current precipitators for analyses of smokes. Warren and Read[11] experienced trouble with the precipitation method for dusts, while Weber[12] has recently shown the usefulness of a device, like Strong's, for determining acid mists.

If the apparatus for this general type of work is to be portable, it must be of reasonable weight. To some, a portable apparatus implies a device that can be carried in one's pocket; to others, an apparatus the size of the Orsatt for gas analyses; while still others are willing to use an equipment weighing 50 lb. or more, particularly if two observers work together. While no one would care to carry a 50-lb. apparatus into an inaccessible place in a mine, it may be perfectly satisfactory for work in a factory where current is available. Where current is not available, the lighter storage-battery outfits can be used and determinations made without the use of any current other than that from the battery.

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[6] M. Shibusawa and Y. Niwa: A New Electrical Precipitation Treater. *Jnl. Am. Inst. Elec. Engrs.* (1920) **39**, 890.

[7] S. H. Katz, E. S. Longfellow and A. C. Fieldner: Efficiency of the Palmer Apparatus for Determining Dust in Air. *Jnl. Ind. Hyg.* (1920–21) **2**, 167; also The Sugar-tube Method of Determining Rock Dust in Air. Bur. Mines *Tech. Paper* 278 (1921).

[8] P. Drinker, R. M. Thomson and S. M. Fitchet: Atmospheric Particulate Matter—II. The Use of Electric Precipitation for Quantitative Determinations and Microscopy. *Jnl. Ind. Hyg.* (1923–24) **5**, 152.

[9] J. P. Baumberger: The Amount of Smoke Produced from Tobacco and Its Absorption in Smoking as Determined by Electrical Precipitation. *Jnl. Pharm. & Exp. Therapeutics* (1923) **21**, 47.

[10] H. Salmang: Ueber die Analyse von Rauch. *Ztschr. ang. chem.* (1924) **37**, 97.

[11] P. H. Warren and T. A. Read: Methods and Apparatus for Determination of Dust Suspended in Air. *Proc.* Australasian Inst. Min. & Met. (1922) [N.S.] No. 47, 297.

[12] H. C. Weber: Quantitative Analysis of Mists and Fogs, Especially Acid Mists. *Ind. & Eng. Chem.* (1924) **16**, 1239.

Alternating-current Method of Precipitating Suspensoids

There appears to be a general misunderstanding of the difference between the alternating- and the rectified-current methods of precipitating suspensoids, and an apparent reluctance to admit that efficient precipitation with alternating current is possible. The alternating-current method seems, perhaps, at first sight, to contradict the popular theory of rectified-current precipitation as originally described by Cottrell, Lodge, Walker, and others, and long since proved of great usefulness.

It will be recalled that Cottrell's original plant was built for the recovery of sulfuric-acid mist—a conducting suspensoid. Small precipitators, like Tolman's, adapted directly from the Cottrell process have been uniformly reported as successful, provided the suspensoid under determination was conducting. When this was not the case, as in the work of such careful investigators as Katz, Fieldner, and Longfellow, or Warren and Read, the results were not so good.

Frequent accounts are given of troubles in rectified-current plants operating on the original Cottrell principle. Often these troubles have been caused by dry non-conducting suspensoids, such as zinc-oxide fume, which pile up on the collecting electrode and materially affect efficient precipitation. To remedy such troubles, the fume is humidified, which renders the particles conducting.

For small precipitators, the alternating-current method, operating on what Strong[13] calls the condensed-field principle, avoids many, but by no means all, of these troubles and is especially suited to our problems because rectifiers are omitted. Rectifiers, whether of the mechanical or thermionic type, like the kenotron, are troublesome and expensive and it is best to adopt a method that does not require their use. It should not be inferred from this that the rectified-current method is not adapted to small precipitators intended for long protracted runs on conducting suspensoids, such as acid mists. Their possible usefulness for such purposes is well demonstrated by the numerous Cottrell plants now working at high efficiencies and has been clearly shown by Baumberger, Salmung, Shibusawa, and Tolman. In discussing the use of small precipitators, like Strong's, for determining acid mists (conducting suspensoids) Weber lays much emphasis on the need of adjusting the vibrator in the induction coil, a manipulation by which Lamb, Wendt, and Wilson found they could increase the positive part of the high-tension discharge and thus more nearly approach the rectified or uni-directional current discharge given by a method such as the transformer and keno-

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[13] W. W. Strong in Bogue's "Colloidal Behaviour" Chap. 23. N. Y., 1924. McGraw-Hill Book Co.

tron. Weber reports having found the authors'[14] pyrex glass tubes "absolutely useless" at the low voltages he employed and used instead thin lead glass tubes, thus again more nearly approaching the rectified-current precipitators. That Lamb and his associates or Weber either required or obtained the degree of rectification given by the kenotron has not been demonstrated.

It is our experience that, in small precipitators intended for runs of short duration, the alternating-current method can be used for both conducting and non-conducting suspensoids. For both long and short runs on non-conducting suspensoids, the alternating-current method, which utilizes the condensed-field principle, is much to be preferred. These facts, which can be very easily confirmed by anyone interested, were established some years ago, especially by the work of Strong to which reference has already been made. The authors' contribution to the use of small precipitators consists simply in adapting proved methods to the solution of their own problems and particularly to the use of the precipitation method for suspensoids to be examined under the microscope.

Constructional Details of Precipitators

The constructional details of small alternating-current condensed-field precipitators, whether of the storage-battery or transformer type, are very similar. These precipitators consist essentially of a suitable device for obtaining high-tension alternating current, a collecting or "passive" electrode, a precipitating or "active" electrode, a suitable device for drawing the air through the precipitator, and a meter for measuring the rate of flow. A rheostat in the primary circuit is advisable, while a ground from the collecting electrode may be used but is not always necessary.

The Collecting Electrode

As shown in Figs. 1, 2 and 3, the collecting electrodes are made of transparent dielectric substances, like quartz or glass, wrapped with a metal foil, such as aluminum. Although we have had no occasion to use electrodes other than glass or quartz, materials such as hard rubber, mica, or bakelite would probably work satisfactorily. While slightly better results are obtained with clear quartz tubes than with glass, they are much too expensive for general use. Ordinary lime-glass tubes are satisfactory for the very small precipitators, particularly if the suspensoid under determination is dry and non-conducting. For the larger precipitators, pyrex is preferred because it possesses higher dielectric

[14] P. Drinker and R. M. Thomson: The Use of Owens' Jet Dust Counter and of Electric Precipitation in the Determination of Dusts, Fumes and Smokes in Air. *Jnl.* Am. Soc. Heat. and Vent. Engrs. (1924) **30**, 695.

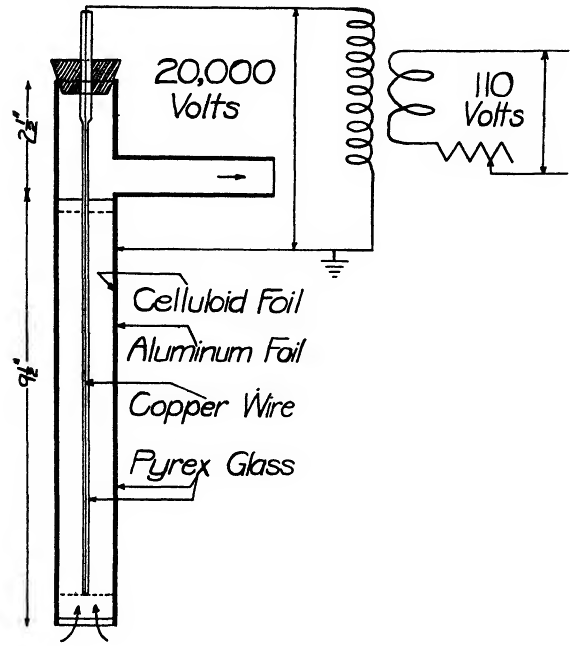

FIG. 1.—TRANSFORMER TYPE OF PRECIPITATOR SHOWING POSITION OF CELLULOID FOIL (SOLID LINE ACROSS TUBE) AND METAL FOIL (DOTTED LINE). COURTESY OF *Jnl.* AM. SOC. HEAT AND VENT. ENG.

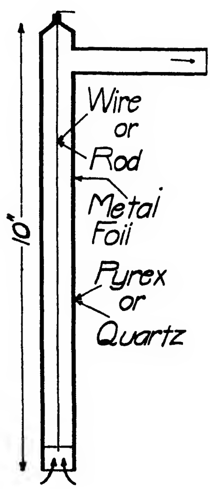

FIG. 2.

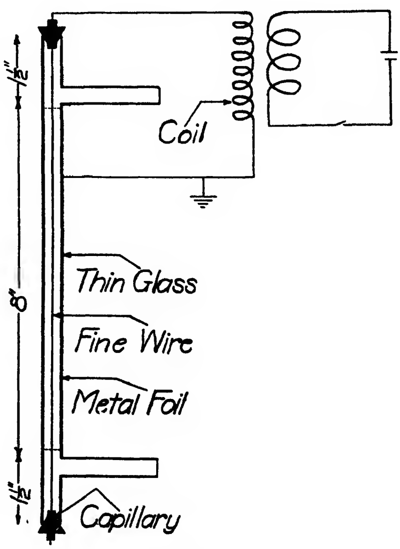

FIG. 3.

FIG. 2.—SPECIAL COLLECTING TUBE USING NO RUBBER STOPPER. COURTESY OF *Jnl. Ind. Hyg*

FIG. 3.—BATTERY TYPE OF PRECIPITATOR FOR DETERMINING DUSTS.

strength than lime glass and is much less apt to be punctured should disruptive discharges take place. For determining acid mists, which are conductors, Weber, as already pointed out, considers pyrex "absolutely useless" and uses lead glass. With dry non-conducting substances, we find lime superior to lead glass.

In both the small and the large precipitators, the optimum diameter of the tube is not sharp. There is always a fairly definite size diameter that, if exceeded, gives poor results, but if smaller diameters are used, there seems to be little change in the efficiency of precipitation. For non-conducting suspensoids, like dry dust or fume, it is best to keep the diameter of the tubes small; for precipitating conducting suspensoids, the diameter of the tube should be made larger, otherwise sparking occurs and the efficiency of precipitation is reduced. For acid-mist determinations, Weber suggests paraffining the inside of the tube so that the accumulated drops run into a glass beaker beneath.

For convenience in handling the precipitate in the laboratory, it is advisable to make the tubes short. Very little advantage is gained by using tubes of lengths comparable to those used in the large-scale rectified-current plants. On the contrary, they are troublesome to clean and are, therefore, a drawback.

The optimum thickness of the walls of the tubes is also questionable and seems to vary roughly with the voltage applied and the dielectric strength of the material used. In the small precipitators, it is best to use thin-walled tubes; while in the transformer type of precipitators, tubes thick enough to obviate chances of puncturing are essential. In any case, there is no trouble caused by slight variations in either the diameter or thickness of the walls of the glass tubes.

Use of Celluloid Foil for Collecting Precipitates

If efficient precipitation has been obtained in small units of either the direct- or alternating-current type, the precipitate is confined to a dense area beginning with the region of the electric field and extending upward but a very short distance. If precipitation has been incomplete, particles extend to the top of the tube. By catching the particles on aluminum foil instead of on the walls of metal tubes, Tolman found that the effectiveness of precipitation could be judged by observing whether or not the precipitate was confined to this dense area at the beginning of the foil. For our purposes, it is better to use transparent foils of low conducting power, such as mica or celluloid, than opaque metal foils like aluminum, although the latter are more satisfactory to weigh.[15] After a run has been completed, the effectiveness of precipitation can be judged

[15] Contrary to our first impression, metal foil on both sides of the walls of the glass tubes gives poor recoveries in the alternating-current precipitators.

by holding the transparent foil to the light and observing how far up the foil the precipitate extends. It is never necessary to run at such low voltages or high air velocities that the precipitate extends to the top of the foil. For testing filtration efficiencies of fabrics, masks, or respirators the celluloid-foil method is especially useful and can readily detect minute amounts of fine fume particles by obtaining their accumulated precipitate over 10- or 20-min. periods.

For the small precipitators, we have been unable to obtain celluloid foil thin enough to fit snugly against the walls of the tubes. Unless the foil fits tightly, precipitation is irregular and often inefficient. With the small precipitator, therefore, efficiency must be judged by the evidences of precipitation at the top of the tube or by the Tyndall effect in the air escaping from the precipitator.

Precipitating Electrode

As in the rectified-current method, the precipitating electrode should be centrally aligned and held rigid; otherwise the area covered by the precipitate is irregular and the precipitation efficiency may be low. In general, better results are obtained when the wire is fine, but it is unnecessary either to thread it, as Tolman did in his rectified-current precipitator, or to use Lamb's electrode with points protruding radially. The wire is inclosed in glass, Fig. 1, in order to hold it in rigid central alignment, to permit the use of copper instead of platinum, and to facilitate the withdrawal of the celluloid foil without disturbing the precipitate. Where the celluloid foil is not used, it is better to use tubes with two side arms (Fig. 3) for the entrance and escape of the air and to hold the wire in central alignment by capillaries inserted in rubber stoppers at each end of the tube. In larger units, like that shown in Fig. 1, there is more than ample capacity, so that it is possible to use the method shown instead of the bare wire, although the latter is the more effective. In the case of the small precipitators, bare wires are advisable because the rate of air flow through the device, at best, is low.

No matter how fine the precipitating wire is made, traces of precipitate are obtained upon it in amounts that vary roughly with its diameter. Often the amount is small enough to ignore, particularly if the sample is taken for microscopic examination and is not to be estimated chemically or gravimetrically. In any case, the removal of these slight amounts is not difficult with either the inclosed- or bare-wire methods.

Fig. 2 represents one of the rather surprising liberties that may be taken with the electrical connections in precipitators for determining non-conducting suspensoids. The precipitating electrode, a fine stiff rod or wire, is fixed in the glass holder at the bottom of the tube, and is held by the constriction in the glass tube at the top. In spite of the contact between the glass holder fused across the tube, and both the

precipitating and the collecting electrodes, this type of tube is satisfactory for both the transformer and the battery type of precipitator.

Suction Fan and Air Meter

An advantage of the precipitation over other methods for suspensoid determinations is the low resistance of the glass tubes to air flow, thus permitting the use of small motors for running the suction fan. For the transformer type of precipitator, a small 110-volt sewing-machine motor may be used, while small motors, run from the batteries, suffice for the smaller precipitators. For use in mines where compressed air is available and current is not, Warren and Read suggest a compressed-air ejector as a source of suction for sampling dusty air.

Whether suction fans or ejectors are used, the rate of air flow is conveniently measured by a device such as the orifice meter or a glass resistance-flow meter. In all cases, the rates of flow can be controlled by rheostats on the motors, by bypasses, or by clamps on the rubber tubing connecting the various parts of the apparatus.

Permissible Rates of Air Flow

As in large plants, it is a simple matter to run the air through the precipitators too fast to catch all the particles. Running the air through too fast, or "overloading," can be detected by the methods already discussed and, in properly made tubes, can be avoided by increasing the intensity of the field or by lowering the rate of air flow, or by both. It is unnecessary to run the precipitators at such high rates that particles escape precipitation.

On the transformer type of precipitator, rates of air flow varying from about 5 to 50 liters per minute are the most convenient. The bulk weight of the apparatus depends mainly on the transformer and varies, in our apparatus, from about 25 to 50 lb. With the lighter types of transformers now available, this weight could doubtless be much reduced. When storage batteries are used, the weight can be reduced to but a few pounds, while the rate of sampling is correspondingly reduced (Fig. 4). With our apparatus the storage-battery method permits rates of about 2 to 8 liters per minute. Strong states that very small precipitators, run from dry batteries, can now be obtained for $8.

Accuracy Attainable by the Alternating-current Method

As pointed out, the alternating-current method of precipitation permits recoveries at efficiencies very close to 100 per cent. Whether the rate of air flow through the apparatus should be measured with a comparable degree of precision, depends on the problem in question. It is difficult, with pitot tubes, orifice meters and similar devices, to measure rates of air flow to an accuracy greater than 95 per cent., and dry or wet

gas meters are too bulky for convenient use in any but laboratory work. Small electric meters, such as are now available for measuring gas concentrations in chimneys and in alveolar air, could doubtless be applied to precipitators. As the accuracy attainable by the precipitation method

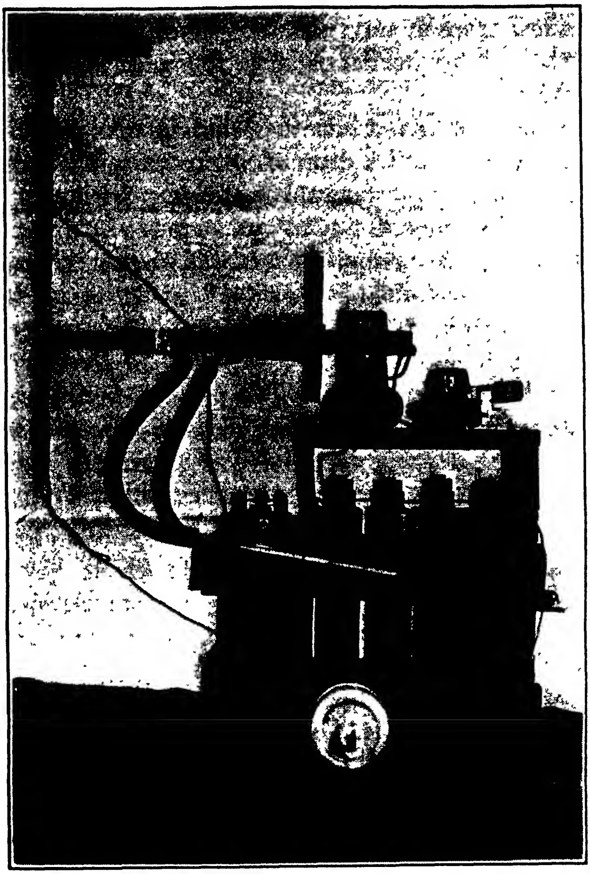

FIG. 4.—PORTABLE STORAGE-BATTERY PRECIPITATOR FOR DETERMINING DUSTS IN AIR; WEIGHT 13 LB.

A, Precipitator tube of lime glass; *B*, flow meter; *C*, suction fan; *D*, motor for suction fan, running on 2 and 8 volts direct current; *E*, radio rheostat controlling speed of motor; *F*, switch for motor; *G*, Ford induction coil; *H*, Edison alkali batteries; *I*, inclined manometer, using ether, for registering pressure on flow meter; *J*, switch on primary of induction coil.

is dependent on the measurement of air flow through the precipitator as well as on the efficiency of precipitation, the individual investigator must choose his method of metering the air in accordance with the precision his problem requires.

Application of Precipitation to Microscopy

By using the celluloid foil, samples may be obtained in a state convenient for mounting and examining under the microscope. Strips are cut from representative portions of the foil and are mounted on glass slides by means of a few drops of amyl acetate. Warming the slide at a gentle heat causes the foil to lie flat against the glass and eliminates surface irregularities.

As the particles are driven into the celluloid with considerable force, it is usually possible to add a drop of oil for examination under an oil immersion lens without disturbing the particles. With many substances, particularly dusts, permanent mounts can be made by fixing the celluloid on the glass slide with the precipitate next the glass. It is often convenient, when using the celluloid-foil method, to withdraw the foil after precipitation and to place it and the precipitating electrode in a glass tube of the same diameter as the pyrex tubes. Packed in this way, the samples can be transported or mailed without disturbing the precipitate, and slides prepared several months after the samples are taken.

Size Distribution of Particles in Precipitate

One of the main advantages we have hoped to obtain by this method is the precipitation of particles in the state in which they occur in air; for example, if the particles were originally flocculated into aggregates, to show them as aggregates, and if dispersed, to obtain them in the same way on the celluloid foils.

We have shown elsewhere[16] that, with the alternating-current method, dust, or flocculated fume particles can be caught at higher rates of air flow than dispersed fumes, while smokes are still more difficult to collect —an effect due probably to the number or concentration of the particles and not to any inherent properties of these different substances. This indicates that the smaller the particles the more difficult they are to precipitate and suggests the possibility that small particles might be precipitated farther up the tubes than large particles. As a matter of fact, however, in complete precipitation of non-uniform substances, such as dust, the precipitate is confined to such a small area that this size distribution is not noticed. As yet, we have obtained insufficient evidence to settle the question one way or the other. It is a matter of interest that Rohmann[17] has found a method of measuring size distribution by utilizing the precipitation principle but employing low voltages. The dispersed cloud is passed through a direct-current field and the

[16] *Jnl. Ind. Hyg.* (1923–4) **5**, 152.

[17] H. Rohmann: Methode zur Messung der Grosse von Schwebeteilchen. *Ztschr. phys. chem.* (1923) **17**, 253.

distance the particles travel before precipitating gives an index of their size.

From the literature on the rectified-current process, one might infer that the alternating-current method would produce mainly flocculation. While such an effect can be shown in a large container filled with a smoke, fume, or dust, conditions in the precipitator are quite different. The time for the particles to pass through the tubes is much too short for them to be caught simply as a result of flocculation. No such effects, moreover, are apparent on microscopic examinations of dry substances precipitated on the foils.

Objections to Precipitation Method

In the transformer type of precipitators, voltages varying from 5000 to 20,000 are used, depending on the suspensoid under investigation. In storage-battery precipitators, the voltage varies from about 1000 to 5000, according to the number of batteries used. The danger from shocks in the transformer precipitators is unquestionably real and not to be dismissed casually. Shocks from the battery type of precipitators are about like those that one gets from the spark plug of an automobile—very unpleasant, but not serious. We have used both types of precipitators constantly during the last three years in both laboratory and field work and see no reason why the voltages employed offer any practical difficulties.

The fact that celluloid foil can be used in the collecting tubes shows that sparking troubles are few, but they do occur occasionally, particularly with wet conducting substances like tobacco smoke. The fire or explosion hazards in small precipitators for dusts like flour, cocoa, hard rubber, bituminous coal, zinc powder, and sulfur are questionable. Trostel and Frevert[18] have shown that to render an air mixture of these dusts inflammable requires concentrations too great to maintain more than momentarily; consequently it is difficult or impossible to suspend in air and then pass a really inflammable mixture of these dusts through the precipitators. In experimental work, no trouble has been experienced from the substances named but we would consider it a needless hazard to use the precipitators in atmospheres where there is the slightest possibility of encountering dangerous dust-air mixtures.

With gases like carbon monoxide, hydrogen sulfide or vapors from alcohol and ether, we have obtained mild explosions in the precipitators. Inflammable gases or readily oxidizable suspensoids should be handled with caution in precipitators of any size and experiments first made in small apparatus at low voltages giving but little ozone and feeble coronas.

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[18] L. J. Trostel and H. W. Frevert: The Lower Limits of Concentration for Explosion of Dusts in Air. *Chem. & Met. Eng.* (1924) **30**, 141.

Summary

The constructional details and adaptation of portable alternating-current precipitators to the quantitative determination of suspensoids such as dusts, fumes, and smokes are discussed. The distinction between the alternating-current method, using glass collecting electrodes, and the rectified-current method, using metal collecting electrodes (Cottrell process) is brought out. Poor results obtained in the past with small precipitators are attributed to failure to distinguish between conducting and non-conducting dusts, fumes, and smokes. A portable storage-battery induction-coil type of precipitator weighing 13 lb. is illustrated in Fig. 4. For taking samples for microscopic study, the authors' method of inserting a celluloid foil in the collecting electrode and catching the precipitate upon it is described. These foils or the entire collecting electrode can be mailed or transported without danger of disturbing the precipitate and representative slides made up later in the laboratory.

Analysis of Performance of a Coal Jig*

By H. F. Yancey† and Thomas Fraser,‡ Pittsburgh, Pa.

(New York Meeting, February, 1925)

The jig may be termed the standard coal-washing machine. Although exact figures on the relative tonnages of coal treated by the various coal-cleaning processes are not available, it is known that a large part of all the coal given special cleaning treatment is handled by jigs. This wide use of the jig warrants a special study of its performance.

In this paper are presented the results of an analysis of work done by a three-compartment jig in treating bituminous coal from the Thick Freeport bed in Allegheny County, Pa. Certain systems of washing coal require sizing before washing, while others treat unsized coal. The prevailing practice, however, for the preparation of coking coal from the more easily washed coal is to treat an unsized or natural feed of about -1 in. size and smaller. Under such conditions, the minimum size of particle that is beneficiated has long been and is still a matter of discussion and conjecture. In a careful laboratory investigation Jüngst[1] concluded that the practical limit of settling of fine coal is reached at from 0.02 to 0.008 in. On the other hand, Hancock[2] has found that single-compartment jigs, used in preparing coal for the domestic market, usually allow most of the heavy (refuse) particles smaller than $\frac{1}{4}$ in. to go into the washed coal. He also states that it is impossible with the ordinary coal jig to make any noticeable improvement in the quality of the coal finer than 20 mesh (about $\frac{1}{30}$ in.). Because of its importance in coal cleaning, the work described in this paper was undertaken for the purpose of obtaining information on this subject, as a part of the general coal beneficiation program being carried out by the Bureau of Mines.

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* Published with permission of Director, Bureau of Mines. Work done in coöperation with the Inland Collieries Co., the Carnegie Institute of Technology, and the Advisory Board of Coal Mine Operators and Engineers of Western Pennsylvania.

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[1] F. Jüngst: *Glückauf* (1913) **50**, 1321; (1914) 6.

[2] David Hancock: *Coal Industry* (1923) **6**, 56.

Plan of Work

A washing test was made on approximately 150 tons of run of mine coal using a three-compartment, double-plunger, Elmore jig equipped with rotary refuse draw valves operated from the jig drive. The length of strokes on the first compartment was 2⅛ in., on the second 1⅞ in., and on the third 1⅝ in. The jig was operated at a speed of 75 strokes

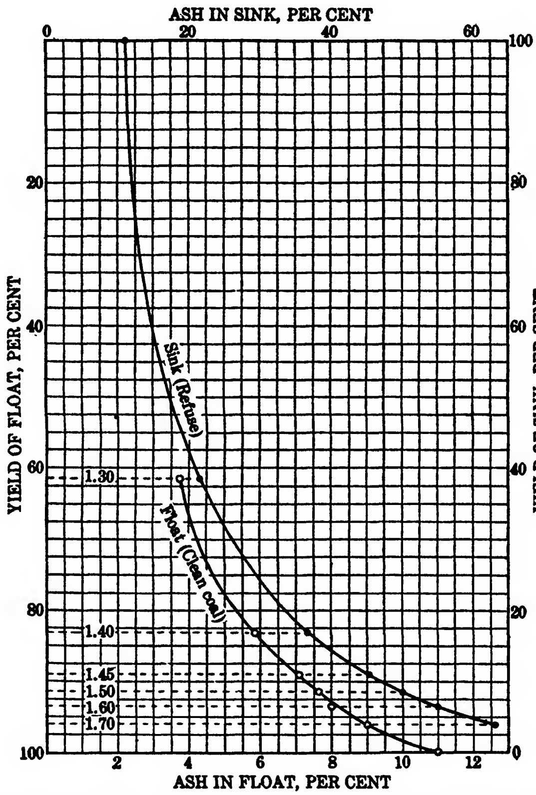

Fig. 1.—Ash content of float (clean coal) and sink (refuse).

per minute. Samples of the raw feed and of the washed coal were taken at regular intervals during the run, the total quantity of each collected amounting to approximately 1200 lb. Screening tests were made on both the raw and the washed coal, and a complete specific gravity analysis, by the float-and-sink method, was made on all the sizes. From these results the percentage removal of impurity was calculated with respect to particle size and specific gravity.

Character of Coal Treated

The Thick Freeport coal may be characterized as one that is difficult to clean both with regard to feasibility and economy. In its raw state

it contains only about 10 per cent. ash and consequently does not require cleaning for steam and domestic uses. For use in the preparation of blast-furnace coke, a reduction in ash by cleaning seems desirable. The run-of-mine coal carries considerable bone coal, having a density between clean coal and refuse, and only 3 to 4 per cent. of refuse material with a density greater than 1.7. The character of the coal treated in the washing trial is indicated by the shorter curve in Fig. 1. The cumulative percentage of float coal on the float-and-sink baths having the specific gravities indicated has been plotted against the cumulative percentage of ash. The longer curve is merely the reverse of the shorter and shows the percentage of ash corresponding to different yields of sink or refuse material. The specific gravity analysis was made on a sample of the raw coal fed to the jig. The size of the feed will be indicated subsequently.

Result of Jig Trial

The general results of the jig run are presented in Table 1; per cent. yield of products and per cent. ash and sulfur are given. The item "loss" refers to material lost and unaccounted for during the test and not to washer loss or shrinkage. An exceptionally long stroke was required with this jig and coal in order to obtain proper stratification of the heavier portion of the bony coal.

Table 1.—*Results of Jig Test (Weights and Analyses on Dry Coal Basis)*

	Weight Pounds	Per Cent. Raw Coal	Per Cent. Ash	Sulfur Per Cent.
Raw coal	306,100	100.0	11.0	0.79
Washed coal (in car)	250,900	82.0	7.8	0.63
First draw	9,280	3.0	55.6	1.45
Second draw	6,780	2.2	46.5	1.07
Third draw	4,440	1.5	34.3	0.99
First hutch	4,370	1.4	27.4	3.72
Second hutch	4,440	1.5	29.0	2.70
Third hutch	6,550	2.1	11.3	0.92
Bradford reject	1,290	0.4	16.3	0.61
Sludge	10,800	3.5	10.8	0.61
Loss	7,250	2.4		
Washed coal and sludge	261,700	85.5	7.9	
Washed coal, sludge, and third hutch	268,250	87.6	8.0	
Calculated ash in raw coal from products			11.1	
Coal (float 1.45) lost in draws		0.6		

Speed, 75 r.p.m.; rate, 41.8 tons raw coal per hour.

The long stroke used gave rather loose beds, which allowed considerable coal to be carried through the screens into the hutch. The loss of

coal in the first hutch was 0.7 per cent. of the feed, in the second hutch 0.7 per cent., and in the third hutch 1.5 per cent. The second hutch product, however, was good secondary coal. The perforations in the screen were ⅛-in. round holes.

If the height of overflow on the jig compartments had been increased so as to maintain a heavier bed on the screens, the loss of coal in the hutches could doubtless have been reduced without impairing the cleaning effect obtained on the finer sizes. In fact, this loss was greatly reduced in another trial when a denser bed was maintained by using a shorter and more rapid stroke, but the larger sizes were not cleaned so effectively.

Screening Tests

Screening tests were made on samples of the raw feed and washed coal. Round-hole screens were used in accordance with a standard screen scale for coal testing work proposed by Holbrook.[3] In this scale the area of any hole is four times that of the next smaller. The smallest screen has holes 1/64 in. in diameter. This screen was not available for the work described here so a 1/64-in. square-hole screen was used instead. The amount and ash content of each size in the raw jig feed and the washed coal are shown in Table 2. The size of opening through which all of the feed would pass is not given but a screening curve indicated that

TABLE 2.—*Screen Test on Raw and Washed Coal, on Dry Coal Basis*

Size, Inches*	Raw Coal		Washed Coal	
	Per Cent.	Ash, Per Cent.	Per Cent.	Ash, Per Cent.
Heads		11.0		7.8
On 1	14.4	15.4	12.8	9.8
1–½	43.8	9.7	44.5	7.8
½–¼	19.1	10.5	21.2	7.5
¼–⅛	9.5	10.6	11.1	7.0
⅛–1/16	5.1	9.8	4.9	5.5
1/16–1/32	3.5	9.8	2.8	5.1
1/32–1/64	0.8	10.2	0.6	5.3
Through 1/64	3.8	11.4	2.1	7.9
Total and weighted average	100.0	10.8	100.0	7.8
Through 1/64-inch on 100-mesh	53.4	11.1	67.6	6.2
Through 100-mesh	46.6	12.3	32.4	11.5

* All screens round hole except 1/64 in., which is square.

[3] E. A. Holbrook: Screen Scale for Coal-testing Work. *Coal Age* (1917) **12**, 396.

it would all pass a 1¼-in. round hole. The run-of-mine coal was crushed to pass 1¼-in. square hole in a Bradford breaker and then passed through a pair of smooth face rolls set at ¾ inch.

Attention is directed to the ash content of each of the sizes of washed coal as compared with the corresponding size of raw coal; a reduction is shown in every case. Even in the size passing through 1/64-in. and retained on the 100-mesh screen the ash content was reduced from 11.1 to 6.2 per cent. The washed-coal sludge was not present in the washed-coal sample on which the screening test was made. An examination of the sludge showed that 95 per cent. of it passed the 1/64-in. screen and that it contained 10.8 per cent. ash. The inclusion of the sludge in the washed coal would, therefore, modify the results given in Table 2, only on the sizes smaller than 1/64 in. The screening tests on the raw and washed coal were conducted by hand, care being taken to minimize breakage.

To obtain additional information as to the minimum size of particle improved by treatment of a natural feed on the coal jig, the raw and washed coal from two other washing trials were examined. The work was done on the same coal and with the same jig that has already been described. The order of the comparative ash reduction was much the same, so that detailed results will not be tabulated, only the percentage reductions in ash being introduced here. In Table 3, column 1, the per cent. ash reductions calculated from Table 2 and the corresponding percentages of material having a specific gravity greater than 1.70 in the raw coal are given. Columns 2 and 3 show the results obtained in the two other trials. The data given in this table indicate that for this particular coal and operation the three-compartment coal jig working on a 1¼-in. natural feed is effective in cleaning particles down to 1/64-in. (square) and quite probably to smaller sizes as well. The figures

TABLE 3.—*Percentage Ash Reduction by Size in Jigging a Natural Feed*

Size, Inches	Test 1		Test 2, Reduction	Test 3, Reduction
	Reduction	Sink 1.70 Sp. Gr.		
On 1	36.4	6.3	19.8	35.6
1-½	19.6	2.7	16.3	23.9
½-¼	28.6	3.8	23.5	26.6
¼-⅛	33.9	4.8	28.0	27.3
⅛-1/16	44.7	5.3	43.6	47.4
1/16-1/32	47.9	5.6	51.6	55.9
1/32-1/64	48.0	5.9	55.6	58.0
1/64-100 mesh	44.3			45.7
100 mesh-0	6.5			26.1
1/64-0	30.7	10.3	33.1	27.1

in column 1 show that, in general, the reduction in ash content is proportional to the amount of impurities present.

Relation of Size and Specific Gravity of Particles to Removal

The introduction of the factor of specific gravity, in addition to size of particle, required the separation of each of the sizes of raw and washed coal into fractions of material according to specific gravity. A complete specific gravity analysis was made of each size of raw and washed coal. Aqueous solutions of zinc chloride were used in separating the sizes larger than 1/64-in., and mixtures of carbon tetrachloride, benzene, and bromoform for the 1/64-in. to 200-mesh sizes.[4] The −200-mesh dust was not treated. The results of this work are shown in Table 4. Using these figures, the percentage of elimination of impurity from the washed coal was calculated for each size and specific gravity class, correction being made for the decreased weight of the washed coal as compared with the raw coal. The results are presented graphically in Fig. 2. The percentage elimination or percentage removal of impurity is plotted against size of particle for several specific gravity classes.

Hancock[5] considers this method one of the best for expressing the efficacy of the washing operation, but the use of such a method requires so much work that probably it will not be employed in routine washing control. However, an investigation of this kind, sufficiently extensive to give conclusive results, furnishes some fundamental data on jig performance that are more or less applicable in any operation. It shows how wide a range of sizes can be effectively treated in one operation. The efficiency of impurity removal may be expected to vary in a measure with the nature of the coal and the separation attempted. The separation obtained in the very fine sizes will, furthermore, depend on the upper range of sizes included, assuming the jig to be adjusted primarily to suit the bulk of the material.

Hancock[6] presents a set of curves, like those shown in Fig. 2 but representing jig performance on a 0 to 3-in. feed, that show very poor impurity removal even of particles heavier than 1.80 specific gravity in the sizes below 1/4 in. This striking difference from the results presented in this paper is attributable to the much wider range of sizes that he attempted to treat, probably with the jig adjusted primarily to handle the larger sizes.

Results such as are indicated by Fig. 2, therefore, may be expected only when treating a size range of 0 to 1 1/4 in. or less. However, this is

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[4] B. M. Bird and H. E. Messmore: Reports of Investigations, Bur. of Mines, Serial 2586, (1924).

[5] David Hancock: Discussion of paper by T. Fraser and H. F. Yancey, *Trans.* (1923) **69**, 476.

[6] *Coal Industry* (1923) **6**, 56.

TABLE 4.—*Specific Gravity Analyses of Sized Raw and Washed Coal (Dry-coal Basis)*

Specific Gravity	On 1-in., Weight, Per Cent.		1- to ½-in., Weight, Per Cent.		½- to ¼-in., Weight, Per Cent.		¼-to ⅛-in., Weight, Per Cent.		⅛- to 1/16-in., Weight, Per Cent.		1/16- to 1/32-in., Weight, Per Cent.		1/32- to 1/64-in. Weight, Per Cent.		1/64- in. to 200-Mesh Weight, Per Cent.	
	Raw	Washed	Raw	Washed	Raw	Washed	Raw	Washed	Raw	Washed	Raw	Washed	Raw	Washed	Raw	Washed
Float 1.30	59.38	66.50	67.71	73.02	70.41	75.93	72.90	77.80	71.25	83.02	72.69	84.38	76.80	84.75	61.24	70.18
1.30–1.40	15.59	19.02	18.09	16.82	14.95	16.32	13.05	14.95	13.97	12.31	12.14	11.96	9.75	11.73	16.41	17.25
1.40–1.50	12.50	12.18	7.22	7.83	6.48	5.58	5.07	4.98	5.37	3.32	5.52	2.42	3.43	2.52	6.02	4.89
1.50–1.60	3.17	1.67	2.34	1.61	2.57	1.56	2.61	1.62	2.49	0.84	2.40	0.63	2.18	0.56	3.54	2.38
1.60–1.70	3.02	0.60	1.90	0.58	1.72	0.42	1.61	0.43	1.62	0.24	1.62	0.28	1.99	0.22	2.42	1.31
1.70–1.80	3.63	0.03	1.02	0.10	1.25	0.14	1.39	0.13	1.22	0.09	1.06	0.16	0.56	0.11	1.61	0.95
Sink 1.80	2.71	0.00	1.72	0.04	2.52	0.05	3.37	0.09	4.08	0.08	4.57	0.17	5.29	0.47	8.76	3.04

a comparatively wide range—as great as is commonly attempted in the preparation of coal for coking. The percentage removal of impurity, as plotted in the graphs, expresses the efficiency of impurity removal in a restricted sense only, as it does not evaluate any loss of coal to refuse during the jigging operation. As an indication of efficiency, it is qualitative rather than quantitative. At first glance, the course of the graphs may appear so irregular and erratic as to preclude the formulation of any general statements, but closer examination will indicate that a number of important conclusions can be reached as a result of this analysis of jig performances.

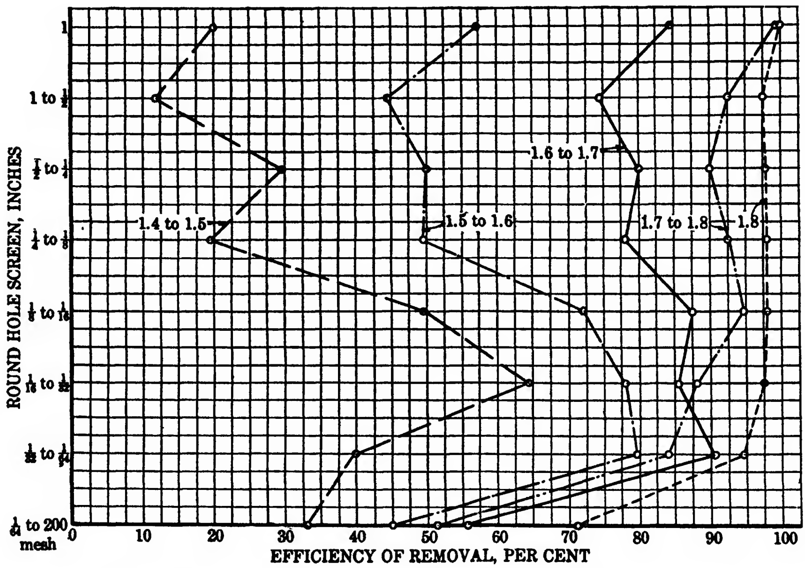

FIG. 2.—RELATION OF PARTICLE SIZE AND SPECIFIC GRAVITY TO REMOVAL BY COAL JIG.

In the first place, the efficiency of removal of impurity becomes more irregular with the decrease in the specific gravity of the impurity; this is to be expected, because there is a decrease in settling ratio. At the lower specific gravities, the graphs are more or less similar in shape and direction. Smooth and fairly regular curves may be drawn through the points representing the removal of material heavier than 1.80 in specific gravity and through those representing removal of the 1.70 to 1.80 specific gravity fraction. All the graphs show a rather marked decrease in removal of impurities on the size between 1 and ½ in.; this size makes up 44 per cent. of the total feed to the jig; more than any other size. Below ⅛ in., for the lower specific gravities, there is a sharp increase in impurity removal; this increase in efficiency continues until the 1/64-in.

size is reached and may be due to the fact that the jig screens have 1/8-in. perforations, at which size two means of egress of impurity become available—the draw valve and the jig screen.

These apparently anomalous results—showing a better separation of the fine particles below 1/8 in. in size than of the 1 to 1/2 in. size—is further explained by the fact that the fine material contains much the larger percentage of impurities available for removal. The 1 to 1/2 in. fraction, while making up a very large part of the feed contains less dirt than any other size. It has been pointed out in a previous paper[7] that the apparent effect in a coal-cleaning machine is to reduce the percentage of free impurity of high specific gravity to a given minimum amount that is more or less independent of the amount originally present in the raw feed. The results of the present work corroborate this earlier conclusion. The fine material between 1/64 and 1/8 in. in size and the larger material of 1 to 1/2 in. in size tend to reduce to approximately the same content of residual free impurities, and, consequently, the fines, being much dirtier to start with, show a greater percentage removal of impurities.

Conclusions

A careful examination has been made of the relation between the size and specific gravity of impurities in relation to their removal by the coal jig.

This study of jig operation shows that when properly adjusted a three-compartment jig will effectively remove free dirt from an unsized feed ranging from 0 to 1 1/4 inches.

When adjusted to work most satisfactorily on such a feed, the jig used for these experiments draws down some good coal with the fine refuse into the hutches. Considering the bony character of the raw coal, the total loss of coal in the rejects is not excessive in comparison with jig performance under like conditions at other washeries that the writers have studied. The advantages of separate treatment of the fine coal would be a slightly increased yield due to recovery of some of the fine coal lost in the jig hutches. This could be accomplished by retreatment of the hutch products on coal-washing tables. By sacrificing some fine coal, the jig can be successfully used to clean coal as fine as 1/64 inch.

[7] *Trans.* (1923) **69**, 452.

Coal Washing Practice in Alabama

By H. S. Geismer, Birmingham, Ala.

(Birmingham Meeting, October, 1924)

Campbell,[1] in 1896 said: "The Birmingham district in Alabama has certain great advantages for there are few places in the world where fuel and ore are so near together, although, unfortunately, both are of inferior quality; the ore being low in iron and high in phosphorus and the coal giving a weak and impure coke."

This statement could not have been questioned in 1894, but by 1896 several Robinson-Ramsay washers had been put into operation and weak and impure coke was a thing of the past.

The Warrior coal field of Alabama contains six seams that yield coking coal of excellent quality. In descending order, they are Brookwood, Milldale, Pratt, America, Mary Lee, and Black Creek. In each of these, however, bands of rock and bone coal of varying thickness are stratified with the coal; and while some of these impurities can be separated from the coal by the miner, much of it must be loaded out with the coal. Consequently, unless the coal is washed before being coked, it will yield a coke of varying ash and sulfur content quite unsatisfactory for blast-furnace use. At present, the Gulf States Steel Co. is producing run-of-mine coal at its Virginia mine, from the America seam, that is uniformly low enough in ash to permit of coking without washing, but this is the only exception to the above statement.

Alabama was the first state to experiment seriously with coal washers, was the first to install washers on a large scale and, up to the present, has maintained the lead. The Alabama State Mine Inspector reports that during 1923 20,919,303 tons of bituminous coal was mined in Alabama; 12,858,499 tons of which was delivered to coal washers for treatment.

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[1] Harry Huse Campbell: The Manufacture and Properties of Structural Steel, 19. The Scientific Publishing Co., New York.

Just now two new systems of coal cleaning are attracting attention in the United States; *i. e.*, the air or dry-cleaning process and the Chance sand-liquid method. Neither of these has been tested in Alabama but with these two exceptions all the methods used for cleaning bituminous coal have been largely brought to perfection in this state.

History of Coal Washing in Alabama

The first attempt at coal washing in Alabama was in 1890, when an experimental Luhrig jig was built at the Birmingham City furnace plant of the Sloss company. A few years later, a Stein washer was built at Brookwood. In 1894, Erskine Ramsay, chief engineer of the Tennessee Coal, Iron & Railroad Co., experimented with a Robinson washer (an English invention) adding to it a sludge tank of his own design. Within the next few years, a number of these plants were built and the Robinson-Ramsay washer, as it came to be known, revolutionized coal preparation in Alabama.

In 1900, Ellwood Stewart, the inventor of the jig that now bears his name, erected a washing plant at Brookwood; the results obtained were so satisfactory that within two years this type of jig became the standard in the state and no more Robinson-Ramsay washers were built. There was not a great deal of difference in the results obtained with these two types of washers, but the Stewart jig had a much larger capacity on the basis of first cost and floor space and required much less water. At present, there are no Robinson-Ramsay washers in operation in Alabama but there are several of the original Stewart washers.

In recent years, practically all of the plants designed to produce coking foal have used two- and three-compartment jigs, mostly of the Elmore type, while the companies producing washed coal for commercial purposes cavor single-compartment jigs; the Montgomery, Stewart, and Elmore jigs predominating in that field. It is not the purpose of this paper to discuss the design or merits of the various jigs but experience with Alabama coals has demonstrated that there is little difference in the quality of the washed coal produced on the different jigs if they are intelligently operated; there is, however, a wide variation in the amount of water required and the percentage of coal lost in the refuse.

The Sludge Problem

When the first washers were built in Alabama, coal costs were low and the land surrounding the mines was owned principally by the operating companies. All fine coal was considered a necessary part of the sludge, and was allowed to find its way to the nearest stream, down which it traveled or lodged along the banks. Increasing coal costs made it advis-

able to recover the fines and damage suits, instituted by the farmers upon whose lands the sludge was deposited, made it necessary to keep the sludge at the plant. This brought up the first problem in connection with coal washing.

The first attempt at a solution of the problem was the construction of settling ponds or basins. The sludge was allowed to settle in a pond until the pond was nearly filled, when the sludge stream was diverted to another pond and the fines from the first pond were recovered, by wheelbarrows or mules and scrapers, and used for boiler fuel. This method has long since been abandoned.

At present, three methods are used for recovering the fine coal from the sludge and for clarifying the sludge-carrying water:

1. Long settling or clearing tanks with slowly moving conveyors dragging (to the discharge end) the fines that settle along the bottom. This is the most common method, but where large capacities are treated it often requires all night operation of the conveyor, at considerable expense, to recover the fines that have accumulated during an 8-hr. shift, and several carloads of wet fine coal are delivered to the washed-coal bin to mix with the regular washed product of the previous day's operation. If the bin is large, this is not particularly objectionable as the fine coal is distributed over a large area; but where the bin is not large, this fine coal may lodge almost as a solid mass in one part of the bin and from there find its way intact into coal cars; holding a mass of this coal in a railroad car is some problem.

2. Pumping all the overflow water from the washed-coal settling tank (this water contains all the sludge) to an elevated conical tank. The water is recovered from the top of the tank and flows back to the sump where the main circulating-pump suction is placed. The fine coal and the fine impurities are drawn off at regular intervals from the bottom of the tank and carried, by a conveyor, to the top of the washed-coal bin. This method was perfected by Robert Hamilton, consulting engineer of the Tennessee Coal, Iron, & Railroad Co., and is used at all the washing plants of that company. The Woodward Iron Co. has also adopted this method. The conical tank is far superior to the long horizontal tank, inasmuch as it does away with the expensive conveyor and there is nothing connected with it to get out of order. Frequent shutdowns of the entire plant may follow breaks in the chain where drag conveyors are used.

3. To date, two installations of Dorr thickeners are to be found in Alabama; one is at the Palos plant of the Republic Iron & Steel Co., where coking coal is produced, and the second is at the No. 2 Overton plant of the Alabama Fuel & Iron Co., which produces steam coal. The fines recovered by the Dorr thickener at Overton have no commercial value, as they run high in rash and fireclay, but the washing plant is located

near a large river and it was considered advisable to prevent the sludge being carried to the river with the waste water.

The Dorr thickener is too well known to require a description; it delivers practically clear water back to the circulating system and is under complete control at all times. The elevated conical tanks used by the Tennessee company, however, seem to remove enough of the fines to allow the water to be used over and over again; the first cost of the tanks is much less and they reduce the size of the plant considerably in comparison with the plant using Dorr thickeners.

In many localities, a distinction is made between fine coal and sludge but this is not the case in Alabama. At all the Alabama operations where coking coal is produced, the sludge consists of water, pure fine coal, and fine impurities, but the percentage of impurities is not large and it is not necessary or profitable to attempt to separate them from the fine coal. At some of the operations in the non-coking fields, the sludge contains a large percentage of rash and fireclay; in that case, the material passing 20-mesh is worthless and no attempt is made to recover it. This is the case at the Overton plant.

It has always been assumed by coal-mine operators and owners of farm lands that the waste water from coal washers was injurious to farm lands because of the fine coal and sulfur that it carried in suspension. During the latter part of 1923, tests were carried on by the Agronomy Department of the Alabama Experiment Station to determine the effect of water from coal washers on farm lands along Lost Creek. These experiments were undertaken at the request of the Galloway Coal Co., which has a washer discharging water into Lost Creek and which at times overflows the land along this creek. The conclusions arrived at were as follows:

1. Corn in cultures of Lost Creek soil made just as good growth when watered with Lost Creek or washer water as when watered with distilled water.

2. The addition of varying amounts of sludge from the coal washer at Mine No. 15 of the Galloway Coal Co. had little or no influence on the growth of corn on soil collected along Lost Creek.

3. Acid phosphate applied at a rate of 600 lb. per acre more than doubled the growth of corn on Lost Creek soil cultures, the same treatment producing only a small increase on the soil from the Experiment Station farm.

4. Water from Lost Creek or from the coal washer at Mine No. 15 of the Galloway Coal Co., is not toxic to corn or velvet beans in water cultures.

5. Neither of these waters contain anything that would injure the growth of corn on lands flooded by Lost Creek.

Of course, one would not be justified in assuming that these conclusions hold for all coal washers on all soils in the United States, but we can

assume that most of the conclusions covering the destructiveness of waste water from coal washers have been without foundation. A complete report of these tests was published in the *Dixie Manufacturer* of Dec. 10, 1923.

Size of Coal Delivered to the Jigs

There is considerable variation in different states as to the size of coal delivered to jigs and the method of reducing the run-of-mine coal to the sizes required. In Alabama, the different plants have pretty well adopted one standard. Plants producing steam or commercial coal almost invariably screen all the coal as it comes from the mine and wash only the coal that passes through the perforations on the screen. Generally the perforations are 2 in. but occasionally 3-in. perforations are found. Such plants do not require crushers. To meet the growing demand for stoker coal, undoubtedly, in the near future some of the commercial mines may decide to crush all their coal and sell the entire output as crushed washed coal. Plants producing coking coal almost invariably crush and wash their entire output; at two large modern plants however, they screen the coal as it comes from the crushers and bypass the fines, washing only the balance of the product.

Double two-roll crushers have been generally used for the crushing. Several hammer crushers were installed in the early days but they produced too large a percentage of fines and complicated the sludge problem. Of late years, Bradford breakers have been installed at most of the large operations to replace crushers. At one plant in particular, the Flat Top washer of the Sloss-Sheffield Steel & Iron Co., one of these machines has entirely replaced crushers and has increased considerably the capacity of the washer, as the breaker serves as a preparatory cleaner and relieves the jigs of some of their work.

At the mines where the entire output of coal is washed, the coal is generally crushed to pass through a ¾-in. ring; this size gives excellent results on plunger jigs of the Elmore or Faust type. With the Stewart and Montgomery jigs, the size of the coal treated has little bearing on the quality of the washed coal produced; in fact, a feed of mixed sizes, from 2½ in. down, gives excellent results. Sizing before jigging as an aid to washing is not attempted at any plant in Alabama; sizing the coal to permit of bypassing the fines has quite a different object.

Chemists at Washing Plants

Because of the large percentage of slate and bone coal found in most of the Alabama coals, officials in charge of properties producing washed coal for coking purposes early realized the necessity of placing chemists

at the coal washers to keep accurate record on the results obtained. It was soon found that these chemists were not only able to improve the quality of the washed coal produced and to keep the product uniform but they were able to reduce the cost considerably. Their tests showed whether an excessive amount of coal was being lost in the refuse (an excessive amount of coal in the refuse always indicated something wrong with one or more of the jigs) as this condition was quickly noticed, it could be remedied before a large loss resulted. For example: If the revolving valve in an Elmore jig should break, considerable good coal might pass off with the refuse without the operator being aware of this loss, unless he was watching the refuse very closely. With a chemist taking samples of this refuse several times daily, the loss is quickly discovered and the necessary repairs promptly made. Running a modern coal washer without a chemist would be like running a modern power plant without recording gages.

After a coal washer has been put into operation, the first point to determine is the ideal analysis for the washed coal to be produced. This sounds easy but it is often a complicated problem and is one that only a chemist can solve. If the plant is to produce commercial coal, a certain analysis for the washed coal has probably been guaranteed and the washer must meet this requirement. This is generally a simple matter, as the chemist is concerned with only one criterion. But if the plant is to produce coking coal, several requirements must be met. Up to a certain point, the ash content of washed coal has little effect on the coal content of the washer refuse, but when that point is passed any improvement in the ash content of the washed coal is quickly reflected in the washer loss. It then beomes a question as to whether the reduced pig-iron cost resulting from lower ash coke will more than offset the higher cost of washed coal. If the coal mine and blast furnace are owned by the same company, an endless argument between the two departments is inevitable, but the company chemist alone has the correct answer.

Construction Material for Coal Washers

In the early days, all buildings around coal mines were constructed of wood and the first coal washers were made of the same material. Gradually steel and concrete replaced wood for all mine buildings including coal washers. There is much difference of opinion as to whether concrete, cast iron, or structural steel is best suited for jig tanks and all three have their advocates. Steel plates are not satisfactory if the water being circulated in the jigs is corrosive; but if the circulating water is not corrosive fairly heavy plates have been found satisfactory. In the modern plants fireproof construction is used throughout.

DATA COVERING REPRESENTATIVE PLANTS

The four large iron-producing companies of the Birmingham district have done much experimenting with coal washers and data covering one washing plant of each company have been furnished.

Woodward Iron Co. Coal Washer, at Woodward Byproduct Plant

This plant handles Pratt seam coal from the company's mines at Dolomite and Mulga. The flow sheet, Fig. 1, shows that all the raw coal goes through Bradford breakers and the material rejected by the breakers is carried to the refuse bin. The material passing the breaker perforations is delivered to a battery of Hummer screens. The material passing through the screens (3/16 by 1/2 in. slots) bypasses the jigs and is taken directly to the washed-coal conveyor. Approximately 30 per cent. of the total run-of-mine coal is bypassed in this manner. The jig plant consists of four three-cell Faust jigs. Although the primary jigs are of the three-compartment type, a secondary product is not produced, the refuse from the third cells and the third hutches is handled in a battery of rewash jigs and the resulting washed product goes to the primary washed-coal bin. Two cone settling tanks are installed at this plant. As this plant is located within a few hundred feet of the byproduct ovens, the coal is dewatered in three Elmore dryers; it has been found that one of the dryers handles approximately 70 per cent. of the total washed-coal produced.

The following figures have been furnished by the operating department of the Woodward Iron Co.:

	Volatile Matter, Per Cent.	Fixed Carbon, Per Cent.	Ash, Per Cent.
Raw coal (coal sent to Bradford breakers)...	26.77	63.52	9.91
Bypass coal (coal from breakers passing through 3/16 by 1/2 in. slot, going to coal bin without washing)....................	28.03	66.43	5.54
Coal to jigs (coal from breaker remaining on 3/16 by 1/2 in. screen)..................	25.96	62.15	11.89
Coal from jigs (average from 4 Faust jigs for year ending May 1, 1924).............			5.52
Coal from rewash jigs (average for year ending May 1, 1924)....................			9.46
Washed coal (a mixture from all jigs and bypass coal)............................	27.95	66.05	6.00

Refuse for the year, ending May 1, 1924, contained 3.21 per cent. float; the ash in the float was 6.58 per cent. The specific gravity of coal

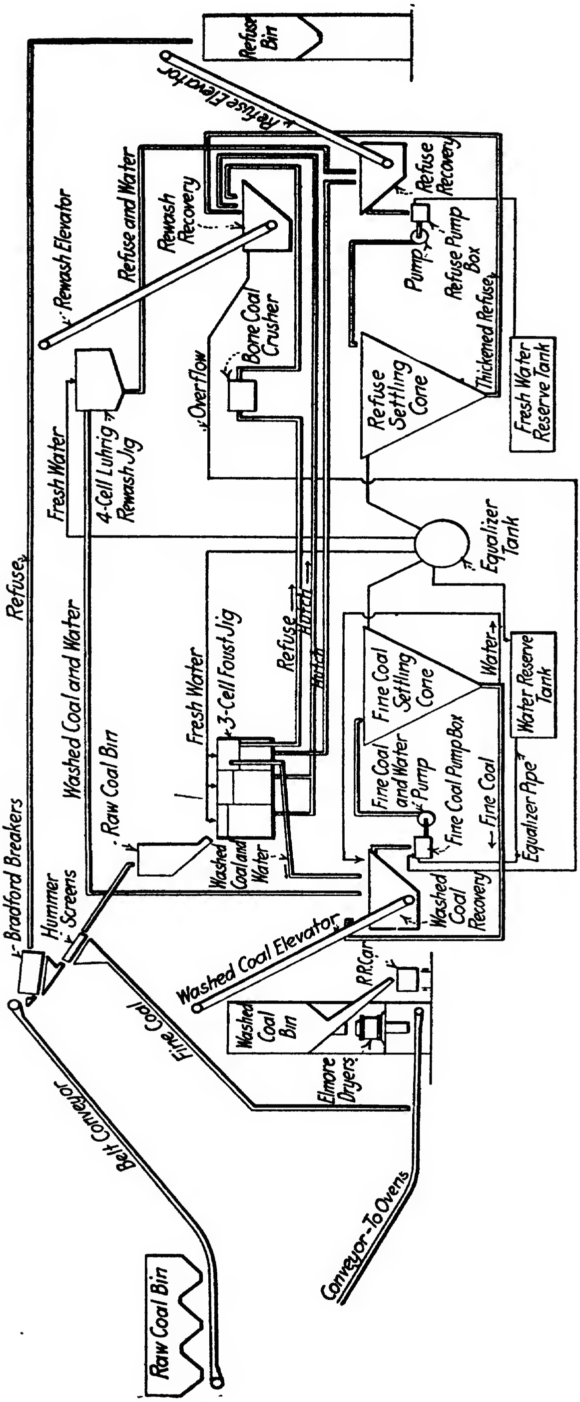

Fig. 1.—Flow sheet, coal-washing plant of Woodward Iron Co.

is taken as 1.37. The screen test on coal from elevators (coal from all jigs) is

On	0.747-in. opening	5.9 per cent.
On	0.525-in. opening	8.3 per cent.
On	0.263-in. opening	24.5 per cent.
On	0.093-in. opening	71.9 per cent.
Through	0.093-in. opening	28.1 per cent.

The amount of water kept in circulation, per ton of coal washed, is approximately 950 gal.; amount of makeup water added, per ton of coal washed, is approximately 41 gal.

Risco Plant of Republic Iron & Steel Co.

This plant handles Mary Lee seam coal from the company's Risco mine. The plant consists of three two-compartment jigs of a modified Elmore type, having Elmore type revolving valves but specially designed plungers. The jigs are constructed of cast iron and cast steel throughout; each has a normal raw coal capacity of 70 tons per hour.

This plant has more elaborate equipment for the preparation of the coal back of the jigs than any plant in the district. The flow sheet, Fig. 2, shows two rotary dumps. The rotary dump on the right is used only when it is desired to inspect the contents of a mine car, to see if the miners are loading dirty coal. Ordinarily the entire output goes through the rotary dump on the left. From this dump, the coal is fed to a Marcus screen by a reciprocating feeder. The fines from the Marcus screen, passing through 1-in. perforations, are carried directly to the main belt conveyor; the balance of the product goes through a large single-roll crusher, then through a double-roll crusher and on to a shaking screen having 1-in. perforations. All coal passing the 1-in. perforations is conveyed by a belt to a set of short-stroke quick-acting screens having 3⁄16-in. perforations and the material passing through the 3⁄16-in. perforations can be made to bypass the jigs; the balance of the material is delivered to the jigs.

The upper left-hand corner of the flow sheet shows that provision has been made for loading the entire output without washing; in that event, by manipulating the valves on the Marcus screen, any of the following grades can be produced: Lump coal, nut coal, lump and nut mixed, run-of-mine.

The circulating water overflowing the settling tank, carrying in suspension a large amount of fine coal, is pumped to a 70-ft. Dorr thickener, set at an elevation above the jigs on near-by high ground. Two of these thickeners have been installed, the extra one to be used as output increases; this was the second Dorr installation to be made in

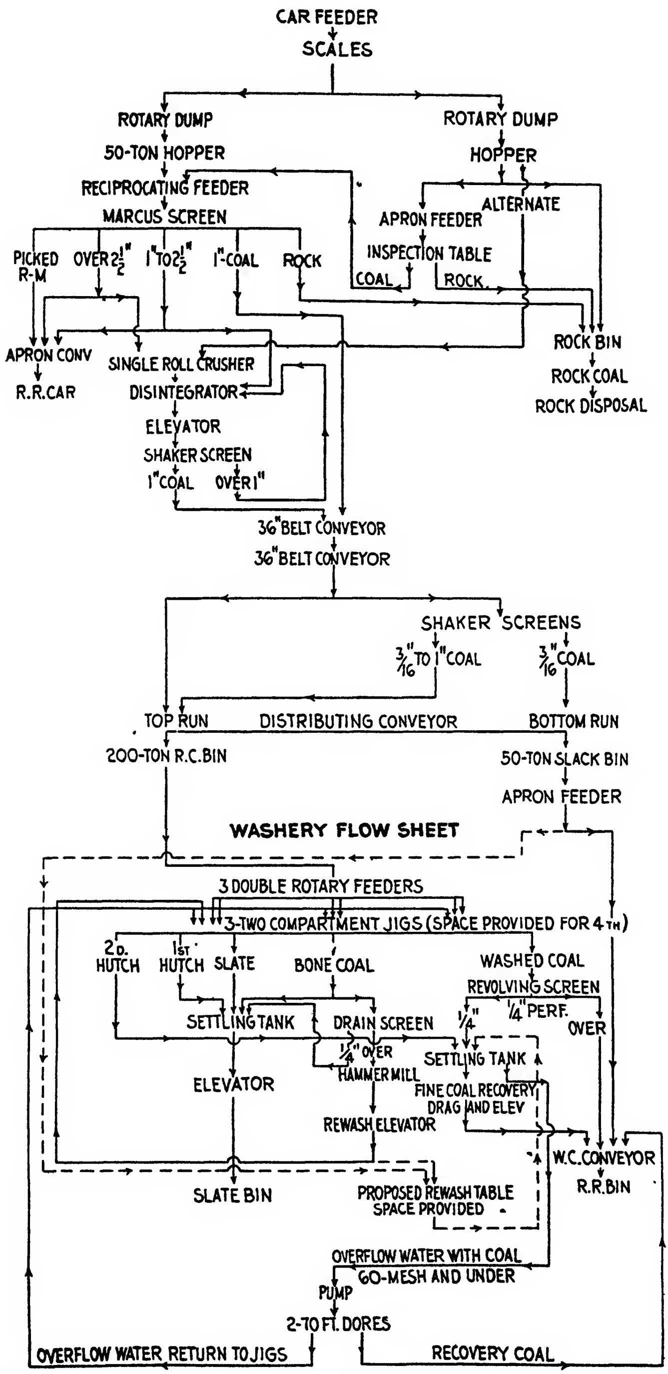

Fig. 2.—Flow sheet, Risco coal-washing plant of Republic Iron & Steel Co.

connection with coal washers, the first installation being at a mine in New Mexico. The clarified water from the Dorrs returns to the jigs by gravity. This feed water to the jigs is, by special arrangement of piping, fed either to the top or underneath the plungers or to both places, as best practice requires. The recovery of fine coal from the Dorr, consisting of 50 per cent. solids or coal and 50 per cent. water, is sluiced to the main washed-coal conveyor thence to washed-coal railroad bin. The Dorr recovery, being 50 per cent. water, falls on the coarse washed coal, the water filtering to the bottom of the washed-coal drag conveyor, in the trough of which are three sections of thin copper plate perforated with fine slotted perforations which allows all water free of coal to return to the settling tank.

The operating officials of the Republic Iron & Steel Co. have furnished the following information.

Due to the fact that the output of Risco mine has not been up to full capacity of the present jig equipment, rewash tables have not been installed and no thorough test of washer efficiency has been made. However, the following tests from our operation show approximate results obtained from tests made on reduced capacity. Adopting 1.35 as the specific gravity of pure coal, the percentage of coal and impurities in the product going to the washer are as follows:

FLOTATION TEST OF RUN-OF-MINE CRUSHED COAL WITH ANALYSIS

	Class, Specific Gravity	Amount, Per Cent.	Ash Content, Per Cent.
Pure coal	1.35	78.7	7.28
Impure coal	1.35–1.40	4.7	14.19
Impure coal	1.40–1.45	4.3	18.24
Impure coal	1.45–1.50	2.4	22.13
Impure coal	1.50–1.55	1.2	28.51
Impure coal	1.55–1.75	1.5	35.85
Impure coal	1.75 and over	7.2	72.14

The average analysis of run-of-mine crushed coal is: Volatile matter, 27.75 per cent.; fixed carbon, 55.50 per cent.; ash, 16.75 per cent.; sulfur, 0.90 per cent.

Average quantities, by sizing test, is as follows:

Size	Per Cent.	Per Cent. Float at 1.35 Specific Gravity	Per Cent. Float at 1.35–1.45 Specific Gravity	Per Cent. Float at 1.45–1.55 Specific Gravity	Per Cent. Float at 1.55–1.75 Specific Gravity	Per Cent. Sink at 1.75 Specific Gravity
1 in.–3/4 in.	18.8	60.7	12.6	3.9	3.3	18.9
3/4 in.–3/16 in.	45.1	79.0	9.9	3.9	2.6	4.6
3/16 in.–20 mesh	27.0	89.5	3.5	1.9	1.6	3.5
Through 20 mesh	9.1	89.6			10.4	
Whole sample	100.0	79.7	7.8	3.0	3.2	6.3

The average analysis of the washed product is: Volatile matter 28.50 per cent., fixed carbon 62.25 per cent., ash 9.25 per cent., sulfur 0.80 per cent.

Loss of coal of 1.40 sp. gr. in refuse, averages about 1.4 per cent. This can be materially reduced by rewashing the crushed bone coal on tables, as contemplated in the original plans of the plant. Total washer loss is 8.5 per cent. to 9.5 per cent. refuse.

Since this plant has been in operation, the mine has been producing coal largely from narrow work. Machine cutting on the narrow work on the bottom increases the amount of impurities in the fines, therefore, there has been no opportunity to by-pass the 3/16-in. coal without washing and it is not possible to say if this plan will be feasible when a larger amount of coal is received from the mine. However, in the design of the plant it was arranged that should the 3/16-in. coal be too high in ash, this product, together with the recrushed bone coal from the second-compartment jig, will be washed over tables. This should insure almost a 100 per cent. recovery of coal in this washery.

By using the Dorr thickeners, all fines from 60 to 200 mesh are removed automatically from the circulating water. Tests made in another plant show that return water from the Dorrs carried only 0.15 per cent. solids, the same water going to the Dorrs carrying 6 to 8 per cent. solids. The ash in the final product, using the tables to be installed, should be reduced to 8 or 8.25 per cent., as against a theoretical 7.28 per cent. ash at 1.35 sp. gr.

Water circulated per jig is approximately 1300 gal. per min., the capacity per jig is 70 tons per hour. Feed water added to the plant is equivalent to the amount moisture loaded in the coal, that is, about 10 per cent. when the draining conveyor is not operating; this is equivalent to approximately 25 gal. per ton of coal washed. When the draining conveyor is operating, there is practically no water lost at the plant as coal is loaded out to approximately 8 per cent. moisture.

Analysis of the recovery from the Dorr thickeners averages approximately 1 per cent. higher than the ultimate washed-coal product; and amount recovered is approximately 5 per cent., by weight, of amount water circulated continuously. By operation of the Dorrs, no fines are pumped back into the jigs or under the plungers to be carried out in the slate or hutch draws and the circulating water is kept free of a cumbersome load of fines that, without the Dorr, build up to 11.3 per cent., by weight, of the water circulated.

Sloss-Sheffield Steel & Iron Co. Washing Plant, at Flat Top Mine

The Flat Top mine produces Mary Lee seam coal and the entire output of the mine is crushed and washed. The plant contained, originally, crushing rolls and six two-compartment double-plunger jigs made by American Coal Washer Co. They are modified Faust type jigs having the driving mechanism located below the jigs.

For several years, previous to 1921, the average yearly run-of-mine output was 408,716 tons and the washed-coal produced averaged 9.88 per cent. in ash; the refuse from the washer contained 8 per cent. good coal. In 1921, it became necessary to increase the capacity of the mine; but neither the crushing plant nor the jigs could handle an increased output satisfactorily.

A Bradford breaker was installed and the two-compartment jigs were converted into single-compartment jigs of double length. For

1922 and 1923, the average output of the mine was increased to 604,346 tons. The ash content of the washed coal averaged 9.11 per cent., and the loss of coal in the washer refuse ran 9.1 per cent. Unfortunately, the changes were made simultaneously and it is not possible to determine just how much of this increased capacity resulted from the installation of the Bradford breaker and how much from the change in the jigs, but the company's engineers are satisfied that the change in design of jig has increased its capacity.

With the six jigs as originally installed, five jigs were used for primary washing and the sixth jig was used to rewash the slate and hutch from the last compartments of the five jigs. Under the new arrangement, all six jigs are used as primary jigs, as no rewashing is necessary.

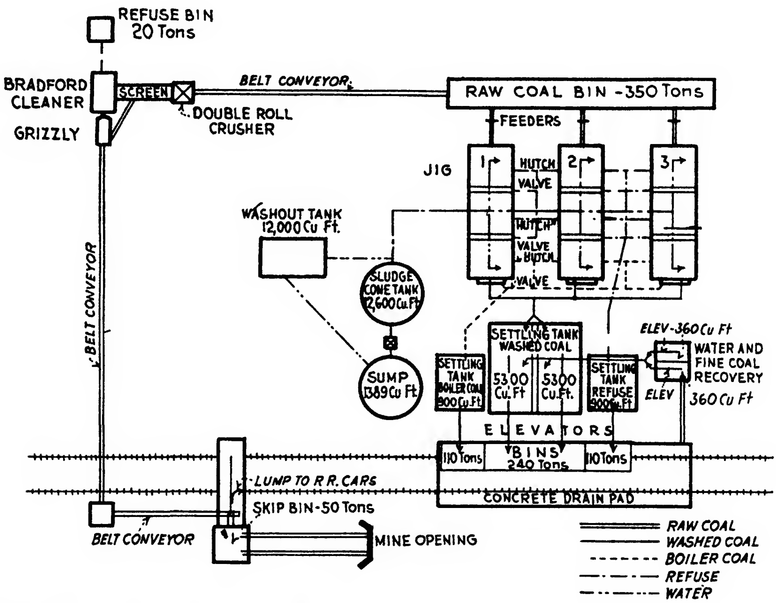

Fig. 3.—Flow sheet, Bayview coal-washing plant of Tennessee Coal, Iron & Railroad Co.

Tennessee Coal, Iron & Railroad Co. Washer, at Bayview Mine

This plant handles only Pratt seam coal from the Bayview mine. The plant contains three three-compartment Elmore jigs; a flow sheet is shown in Fig. 3. The run-of-mine coal is first taken to a Bradford breaker, where the coal passing through the breaker screen has been crushed to ¾ in. and under, and is then delivered to the jigs. In normal operation all the sludge is carried to the top of this tank.

If any delays occur, such as might be caused by the breaking of an elevator or a main supply water line, all the circulating water from the

washing plant is immediately drained to a sump in the ground just in front of the cone sludge tank. When the plant is ready to resume operations, this water is elevated into the sludge tank and operations are begun. This sump is necessary because all the drainage from this washing plant finds its way to the main water supply of the company's furnace and steel plant at Ensley, so every precaution has been taken to prevent impurities reaching this supply. In a four-day test, it was found that the fine coal carried off by waste water from this washer amounted to only 8.7 lb. per 1000 tons washed coal produced.

The flow sheet shows that provision has been made for loading lump coal but under normal conditions all of the coal is treated in the washer.

Considering the tonnage produced and the quality of the product one cannot fail to be impressed by the small size of this washing plant. This is partly because rewash jigs and tables are not used. The product coming from the last refuse valve on each jig is high in ash but it makes a satisfactory boiler coal so the company has found it cheaper to use this at its boilers (it is only equivalent to 6.53 per cent. of the total raw coal) than to install the necessary rewash jigs or tables.

Not all of the washers delivering coal for coking purposes produce boiler coal but none of them, in Alabama, are using tables at the present time. Several commercial mines have recently installed tables at their washing plants.

For the year 1923 the following results were obtained at this plant; the data were furnished by the engineering department of the company.

	Per Cent.	Tons	Tons
Raw coal delivered to washer			494,733
Washed coal to coking ovens, 1.37 sp. gr.	82.05	405,931	
Boiler coal to steam plants, 1.37–1.56 sp. gr.	6.53	32,295	
Refuse over 1.56 sp. gr., 11.42–5.4 per cent. float	10.81	53,489	
Washer loss, float at 1.36 sp. gr. in refuse	0.61	3,018	
	100.00		494,733

Number of 9-hr. turns in operation	566
Tons of raw coal per turn	874

Proximate Analysis

Coal	Volatile Matter, Per Cent.	Fixed Carbon, Per Cent.	Ash, Per Cent	Sulfur, Per Cent
Raw coal	26.42	61.14	12.44	1.76
Washed coal	28.18	67.06	4.76	1.30
Boiler coal	25.45	59.73	14.82	2.25
Refuse float (5.4 per cent.)			5.19	1.49
Sink (94.6 per cent.)			62.81	4.74

SIZING TESTS

Raw coal	Over ¾ in. 9 per cent.	Note per cent.
Washed coal	Over ½ in. 19 per cent.	of sizes is very
Boiler coal	Over ¼ in. 20 per cent.	variable.
Refuse float (5.4 per cent.)	Over ⅛ in. 14 per cent.	
Sink (94.6 per cent.)	Under ⅛ in. 42 per cent; ash 7.3 per cent.	

Inherent ash in coal at 1.37 sp. gr.	4.2 per cent.
Inherent moisture in coal	3.2 per cent.
Washer efficiency: separation	88.23 per cent.
recovery	99.39 per cent.
Total efficiency	87.69 per cent.

Water in circulation, 600 gal. per ton of coal washed per shift; approximately 970 gal. per min.

Water loss 27 gal. per ton of coal washed.

Average power used 1.24 kw.-hr. per ton washed coal.

DISCUSSION

WILLIAM KELLY, Iron Mountain, Mich.—Is the dry-cleaning method used?

H. S. GEISMER.—Neither the dry-cleaning process nor the Chance sand-liquid method has been tested in Alabama; but all other methods used for cleaning bituminous coal have been largely brought to perfection in this state.

H. D. PALLISTER, Tuscaloosa, Ala.—Have you the results from the recent work on the tables with reference to fine coal?

H. S. GEISMER.—None of the iron-producing companies has adopted the tables, though three commercial operators have installed tables within the last six months. I tried to learn the results, but they were not willing to release the data just now. At the mines producing domestic coal, fines present a difficult problem; until within the past six months all the fine coal was wasted. The operators are trying to recover some of it on the table.

L. E. BRYANT, Rockwood, Tenn.—Is there any connection between the sulfur content of the sludge and the effect of the sludge on vegetation?

MILTON H. FIES, Birmingham, Ala.—The sulfur content is very light. The sulfur was not found to be objectionable when the experiments were made at Auburn, with soil that had been contaminated with washer sludge. As a matter of fact, the growth of plants planted in water taken from the watershed affected was much better than the growth of plants planted in distilled water. I think it was proved that

the water from the particular washer in question had some food value as compared with distilled water. The sulfur in this coal runs very low.

H. S. Geismer.—Occasionally the sulfur in the Pratt coal goes as high as 1.75 per cent.; that is above the average of sulfur content in the coals of this state.

L. E. Bryant.—Probably for 40 years they have been washing what is called Sewanee (sometimes called Nelson) coal; this coal is low in sulfur. No provision is made for putting the sludge in a basin, so it flows off for perhaps 15 miles and deposits on the river bottoms. During the first year or two several suits were brought against the company, which began to buy some of the farms. Recently it has been found that the little lumps of coal, when the coal is low in sulfur, increase the porosity of the soil, giving it a chance to make plant food; the crops are not affected at all. In western Kentucky, where the sulfur is almost equal in heat value to the carbon, the sludge is not beneficial to the soil. I wonder if it was not the sulfur that caused the trouble rather than the sludge.

H. S. Geismer.—Perhaps some chemist could help us on that proposition? Sulfur in the form in which it exists in coal (largely sulfide of iron) is insoluble and, therefore, would do no damage. It is only when the sulfide oxidizes to sulfuric acid that damage is done. Oxidation takes place when coal is stacked or piled and when the sulfuric acid reaches the streams, it causes many troubles. I do not know, though, whether the coal in fine particles in the soil would oxidize, as it would not be subjected to the heat generated in the large piles.

Elmer F. Harris, University, Ala.—The carbon of coal is soft and the oxidation would be very low. If the refuse content is increased, naturally it would facilitate the oxidation of the coal. The fine coal, when deposited on the land, would necessarily have to be there for many years; whether it had food value for plants would not be the only thing that would be considered.

James A. Barr, Mt. Pleasant, Tenn.—Sulfur is one of the needed constituents of fertilizer in California. It is present in the form of gypsum or calcium sulfate. On the alkali lands it is very valuable.

L. E. Byrant.—That might be the solution. It may be that sulfur does damage in the western country. The effluent contains iron, aluminum, and alum; there is little sulfuric acid. The solution corrodes any metal and stops plant growth.

Milton H. Fies.—The trouble with which we must contend is the water that flows from the washer. The washers in this district require from 100 to 150 gal. per min. of make-up water; in some cases where the water is used just once, 1000 gal. per min. is required. The farmers

along the creeks complain that these waters carry fine coal and fine particles of fireclay upon their property, and damage it. We had that water analyzed and found that the water was alkaline; also, by experiments at the State Agricultural College, that in the soil along these creeks, where the deposits of fine coal was thickest, these washer fines would not injure plant growth.

The slate that comes from the washer should not be confused with the fine coal and fine fireclay that is held in suspension in the water flowing down the creek. This water is not high in sulfur because it is the overflow from the settling tanks, the sulfur, being heavier, sinks.

William Kelly.—A little over 40 years ago, I accepted a position at a furnace property on the west border of the Broad Top coal field in southern Pennsylvania. As the coal was thought not to be clean enough for furnace coke, a coal washer had been erected some years before and was in operation, up to a couple of days before my arrival, when it had been closed for the Christmas holidays on account of a shortage of men. Coke from the unwashed coal had therefore been charged into the furnaces, and it was expected that the furnaces would run cold. So we watched the gas, cinder, and iron, but there was apparently no change in the heat of the furnace. It was then suggested that we run through the holidays with the unwashed coal, and after that, if no change in heat became apparent, that we run for two-weeks periods with washed and with unwashed coal alternately to determine if there was any difference in the heat obtained. The change was made as I remember it, three times and then the coal washer was shut down. This effected a saving of nearly 50 cents a ton on the cost of the pig iron.

Later we found that the coal washer had been taking out some of the purest and best coal with the slate, probably just enough coal to melt the slate eliminated. There was not much sulfur in that coal, so there was no other reason for washing the coal. Of course, had the coal-washer problem been met as it is being today, the loss of the fine coal would have been saved, and very different results obtained.

George G. Crawford, Birmingham, Ala.—Does the refuse from coal washers affect the fish in the streams? How many coal mines are on the watershed of the Village Creek reservoir?

E. C. Wright, Tuscaloosa, Ala.—There are six mines and seven washers, but there are so many gold fish in that reservoir that we are glad to have them taken out.

George S. Rice, Washington, D. C.—How much of the sulfur is in the form of pyrites?

Elmer F. Harris.—I have no data concerning that, but at least three-fourths of the sulfur is usually quite well disseminated through the coal. There is some organic sulfur, and a little combined with lime.

R. V. Norris, Wilkes Barre, Pa.—In the older days in the anthracite field of Pennsylvania, we had a very serious stream-pollution proposition. The refuse from the mines was deposited along the streams, and then washed into them so that not merely the streams, but the Susquehanna River to below Harrisburg, had large deposits of coal. An efficient method of prevention is to filter the sludge from the washer through a filter bed, made of the refuse banks themselves; the water comes out very clear from drains under them. When a law requiring the neutralization of the acids from the coal mines was proposed in Congress, one of the anthracite companies found that the amount of limestone necessary to neutralize the acid water from this operation would be considerably more than double the total output of limestone in the United States. It is not a question of putting into the water a few pounds of limestone; it would result in putting an enormous additional cost on an industry that cannot bear it. I do not believe we can have mine waters absolutely free from acids, I do not believe we should be required to, and I do not think that the damage done by the acid waters in streams could compare with the damage done to the country by forcing additional cost on coal production with the resulting increase in price.

Byproduct Coking in Alabama

By F. W. Miller,* Birmingham, Ala.

(Birmingham Meeting, October, 1924)

Prior to the Civil War, there were several small charcoal furnaces for smelting the brown limonite ore that is found, in comparatively small bodies, throughout the central and north-central portions of the state. During the Civil War, these furnaces furnished charcoal iron to the Confederate Government.

No attention was paid to the large bodies of lime-bearing hematite ore that now supplies the bulk of the ore used in the various blast-furnace plants of this district until the latter part of the 19th century. Red Mountain, which is the southernmost and one of the smaller ranges of the Appalachian Chain, lying immediately south of the Birmingham and Bessemer, is the principal source of this ore. The orebody outcrops on the northern face, extends through the mountain, and underlies Shades Valley on the southern side.

When it was found that these ores could be worked satisfactorily in the blast furnaces, there was a comparatively rapid growth in the blast-furnace industry in the Birmingham district. As these ores are far more refractory than the limonite ores, this blast-furnace development was accompanied by the construction of beehive ovens to carbonize the coal, in order to supply the necessary fuel. The state's production of beehive coke in 1880 was 60,781 tons; ten years later this had increased to 1,072,942 tons; and, in 1897 the production had reached 1,443,017 tons. In 1898, the first byproduct oven built in the state was put in operation. This plant consisted of 120 horizontal-flue Semet-Solvay ovens, three flues in height by thirty flues in length with an average width of 16 in. The plant was constructed by the Semet-Solvay Co., for the Tennessee Coal, Iron & Railroad Co., and was located adjacent to the blast-furnace plant of that company at Ensley. Coal was delivered from the Pratt mines, by gravity tracks, directly into bins of the ovens after having

* Manager Byproduct Department, Sloss-Sheffield Steel & Iron Co.

been properly crushed and washed at the mines. The coke was delivered by the Semet-Solvay Co. into coke bins of the blast furnaces directly from the quenching cars.

The coke production in 1898, for the entire state, was 1,663,000 tons; and in 1900, 2,110,837 tons.

In 1902, four additional batteries of Semet-Solvay ovens were added to this plant. These later ovens were of the same dimensions but were four flues in height; that is, the heating wall was 80 in. high instead of 60 in.; and the total coke production for the state increased to 2,552,246 tons.

The plant, as originally constructed, was of the recuperative type; the waste heat passed parallel to the waste gases in the sole flue of the oven, bringing the temperature of the incoming air up to approximately 350° C. The waste heat was then allowed to flow through waste-heat boilers and produced the high-pressure and process steam, together with the electric power required for the complete operation of the plant.

The refractory lining of the early ovens consisted of high-grade fire-clay tile imported from Belgium. These tile blocks were from 20 to 30 in. long, 20 in. high, and approximately 12 in. wide, with a hole of eliptic cross-section running through the block. The blocks were tongued and grooved, to prevent leakage, and were set with high-grade American clay. The division walls between adjoining ones were constructed of standard 9-in. firebrick and, for the coking periods permitted at that time, served their purpose excellently.

This plant, the Belgian tile having been replaced by silica shapes, was operated through the World War, on a coking time of approximately 15 hr. and has maintained an equal or better coking time up to the present. It has a remarkable record for consistency in operation throughout its 26 years and is capable of indefinite operation, although handicapped by the small size of the coking chamber. Its annual capacity is 730,000 tons of dry coal or about 530,000 tons of coke.

In 1906, the Semet-Solvay Co. constructed, for the Central Iron & Fuel Co., at Holt, 40 Semet-Solvay ovens of the cold-air type. These ovens are 100 in. to the coal line, 16 in. average width, and 30 ft. in length. No more byproduct ovens were added until 1911–12, when the plants of the Woodward Iron Co. and the Tennessee Coal & Iron Railroad Co. were constructed.

The Woodward plant consisted of 170 Koppers ovens and 60 Wilputte ovens; the Koppers ovens have an average width of 18¼ in., are 8 ft. 7 in. to the coal line, and 39 ft. long. The Wilputte ovens have an average width of 10¾ in., are 8 ft. 7 in. to the coal line, and 35 ft. 9 in. long. No. 1 battery was built in April, 1911; No. 2 battery in August, 1923; No. 3 battery in December, 1914; and No. 4 battery in November, 1917. This plant has a maximum capacity of 1,760,000 tons dry coal per year.

In 1911, the Tennessee Coal, Iron & Railroad Co. constructed four batteries of Koppers ovens 19¾ in. wide, 8 ft. 6 in. to the coal line, and 37 ft. 3 in. long; the plant at that time had an annual capacity of 2,146,000 tons of coal. In 1920, this company added two batteries of 77 ovens each, bringing the total number of ovens in this plant up to 434 and increasing its annual coal capacity to 3,340,000 tons. This plant now supplies all the coke required by 11 active blast-furnace stacks of the Tennessee Coal & Iron Co. and, in addition, is capable of handling some coke for the commercial market. In 1913, the coke production of the state had risen to 3,323,664 tons, 2,022,959 tons of which was byproduct coke and 1,300,705 tons was beehive.

In 1917, the Gulf States Steel Co., located at Alabama City, placed in run its byproduct plant of 37 standard Koppers ovens, with an annual capacity of 250,000 tons of dry coal. These ovens have an average width of 18¼ in., are 9 ft. 10 in. to the coal line and 37 ft. long. The average coking time for 1923 was 15 hr. 21 min., the plant having been in continuous run since April 17, 1917, with no extensive repairs and with excellent results.

As a result of the stimulus of the World War, the Alabama By-Product Corpn. constructed at Tarrant, a suburb of Birmingham, 50 Koppers ovens having an average width of 16 in.; height to coal line, 9 ft. 10 in.; and a length of 37 ft. The Sloss-Sheffield Steel & Iron Co. began the construction of 120 Semet-Solvay ovens with an average width of 18½ in., height to coal line 11 ft., and a length of 36 ft. These ovens, which have the largest coking chambers of any ovens in the state, have a capacity of approximately 15 tons of coal per oven charged and an annual coal capacity of 970,000 dry tons. In 1923, the Alabama By-Product Corpn. added 25 ovens of the same capacity to the original battery; bringing the annual coal capacity to 456,000 dry tons.

The total coke production of the state for 1923 was 4,200,000 tons, of which 268,000 tons was produced in beehive ovens and 3,932,000 tons in byproduct ovens. This means that less than 7 per cent of the total coal carbonized for metallurgical purposes in the state was carbonized in beehive ovens. It is not necessary to go into the fundamental causes of this rapid displacement of the beehive by the byproduct oven. The byproduct oven represents a much larger capital outlay per ton of coal carbonized, but the byproducts are fully capable of carrying this increase. The more uniform grade of coke, the direct saving of coal through yield of coke, the conservation of coal resources, and the reduction of labor cost, together with more favorable working conditions for labor are the major factors.

It is, however, noteworthy that Alabama, which has always enjoyed a plentiful supply of common labor at comparatively low rates, has outstripped her sister states in her progress in coking.

The annual capacity, in tons of dry coal, for this district:

Tennessee Coal, Iron & Railroad Co., Ensley	730,000
Central Iron & Fuel Co., Holt	330,000
Woodward Iron Co., Woodward	1,760,000
Tennessee Coal, Iron & Railroad Co., Fairfield	3,340,000
Gulf States Steel Co., Alabama City	250,000
Alabama By-Product Corpn., Tarrant	456,000
Sloss-Sheffield Steel & Iron Co., Birmingham	970,000
	7,836,000

It will be noted that the combined coking capacity of all of these plants, if operated at their maximum production rate, will be equivalent to the consumption of 7,836,000 tons. Assuming an average yield of 75 per cent of furnace fuel, these plants will produce annually, 5,362,000 tons of coke. As the maximum amount of coke so far produced in the state in any one year (1917) was 4,892,589 tons, even when allowance is made for improvements in furnace capacity, which have been steadily taking place, the byproduct ovens are capable of producing all the coke required by the state without any assistance from the beehive ovens whatsoever.

There is no district in the United States in which the substitution of the beehive oven has been so complete as in the state of Alabama. The districts of Chicago, Detroit, Buffalo, and a few other points, of course, have no beehive ovens; the development at these points represent a transference of the coking operation from the mine mouth in Pennsylvania, Kentucky, and West Virginia to the point of demand. This transfer has been justified by the production of coke-oven gas for domestic and industrial uses and by making available valuable byproducts nearer the point of consumption.

As the South is proportionately the largest consumer of ammonium sulfate, practically all of the ammonium produced by the Alabama byproduct ovens is produced in the form of ammonium sulfate and marketed to the various manufacturers of commercial fertilizer.

As the Birmingham district is the largest producer of cast-iron pipe in the world, it is also the largest consumer of coal tar for the dipping of the pipe manufactured in this district.

The development of blended motor fuel has probably been carried farther in the Birmingham district than anywhere else in the United States and, consequently, almost the entire production of benzol is consumed within a reasonable radius of Birmingham, by the automotive industry. During the late World War, practically all of this benzol was converted into pure products and consumed by the manufacturers of munitions.

The coke-oven gas from the various plants is largely consumed by industries and municipalities. The plant of the Sloss-Sheffield Steel &

Iron Co. supplies domestic gas of approximately 550 B.t.u. to Birmingham through the Birmingham Electric Co. The Holt plant supplies gas to Tuscaloosa and to the ore-nodulizing plant of The Central Iron & Fuel Co. The Tennessee Coal, Iron & Railroad Co. consumes its gas in its steel plant; in addition, it receives about 6,000,000 to 7,000,000 cu. ft. daily from the Semet-Solvay ovens at Ensley. The Alabama By-Product Corpn. has a 3,000,000 cu. ft. holder, in which it stores the surplus gas produced at night, thus making all of its surplus gas available during the day. This has enabled the company to supply, through a subsidiary pipeline company, gas to the Stockham Pipe & Fittings Co., the American Radiator Co., the Kilby Frog & Switch Co., and the Vulcan Rivet Co.

The Gulf States Steel Co. consumes its surplus gas within its own steel plant, while the Woodward Iron Co. uses its gas under boilers, supplementing its blast-furnace gas to produce steam not only for its furnace plant but to supply power for its mines and other activities.

The members of the Institute will be interested in seeing the boiler and power plant of the Sloss-Sheffield Steel & Iron Co. This plant, located at its byproduct plant, has a battery of eight Sterling boilers equipped to burn coke-oven gas, coke breeze in Coxe stokers, and pulverized coal. This power plant supplies the company's coal and ore mines, its quarry, and two of its furnaces, in addition to its byproduct plant requirements, and sells power to the Phoenix Portland Cement Co. Extreme flexibility is required in order to be able to supply gas to the city in amounts varying over wide limits with the seasons, and to take care of the rapid hourly fluctuations of its mine load.

Inasmuch as the conversion from beehive carbonization to byproduct coking has been so complete, the construction of byproduct ovens will be relatively slower, as it will be forced to follow the development of the blast furnace and steel industry. However, as the South is now consuming the greater part of the iron produced in this district and this southern demand is growing rapidly, additional blast furnaces, and probably steel plants, will be constructed and the construction of byproduct ovens will keep pace with this development.

DISCUSSION

THEODORE SWANN, Birmingham, Ala.—We have been working for about two years on the production of phosphoric acid in an electric furnace, by charging phosphate rock into the furnace. We can make the liquid phosphoric acid, running from 90 to 93 per cent. H_3PO_4 and use it, instead of sulfuric acid, to fix the ammonium liquid produced from the byproduct ovens in this district. We make a product that runs about 60½ per cent. phosphoric acid and about 14½ per cent. ammonium. By using the pure phosphoric acid and pure ammonium, though the

ordinary Grade B ammonia is satisfactory, we can make the phosphoric acid used in the manufacture of fertilizer. Phosphoric acid is the correct thing to use to fix ammonia for fertilizer, not sulfuric acid. If it is desired to reduce the cost, a cheaper grade of phosphoric acid may be made; the heat reaction is somewhat greater. We found a rectangular boiler made out of 2-in. tongue-and-grooved plank, lead lined, with a brick lining inside of that, very satisfactory and efficient.

Belt Conveying of Coal at H. C. Frick Coke Company Mines

By Thomas W. Dawson,* Scottdale, Pa.

(New York Meeting, February, 1925)

The H. C. Frick Coke Co. has used belt conveyers for handling coal for the last eighteen years but, until recently, only for small tonnages and over short distances. The first installations were outside the mines for distributing coal to various parts of plants. A belt conveyer was put in service at Colonial No. 4 Mine in November, 1906, to carry coal from the main hoisting shaft to a storage bin serving two blocks of beehive ovens on the other side of the valley; it was in constant service until the Colonial No. 4 ovens were abandoned less than a year ago. This conveyor was in an overhead gallery that spanned our sidings and yard tracks and the main line of the Pennsylvania Railroad. It was a crude installation, from the viewpoint of present conveyor engineering practice. It had no mechanical feeding device, the coal simply ran through a gate in the side of a bin on to the belt; but one belt on this conveyor lasted eleven years. This conveyor is about 300 ft. long center to center of pulleys. It operated at a speed of 250 ft. per min. and carried about 400 tons per day. On this basis, the belt life of eleven years means that not over a million and a quarter tons was carried by the belt. While this is not a large tonnage, the cost per ton was much less than by any previous method in use for supplying coal to ovens located at a distance from the main shaft.

The next belt conveyor was installed at Bridgeport Mine in 1907. It carried about the same daily tonnage as the first, delivering from the hoisting shaft to a coke-oven bin. Very few data were kept on this conveyor. It also operated until the coke ovens at the plant were put out of blast and the coal taken to the Clairton byproduct plant by river.

In 1916, work was started to equip the Bridgeport, Palmer, Gates, and Ronco mines to load their entire output on the river for transportation to the Clairton byproduct plant, which was then being built. These mines were all operating at that time and had a large area of coal available for river shipment. The Monongahela Railroad was located between the hoisting shaft and the river at each of these plants and, therefore, had to be crossed at each location to deliver coal to the river.

After careful study, it was decided to transport this coal from the hoisting shaft to the river at each of these plants by belt conveyors.

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Bridgeport was designed to handle 2000 tons and the other plants 2500 tons per day each. Bridgeport was provided with a belt 42 in. wide, and each of the others with belts 48 in. wide, all to be operated at a speed of 300 ft. per min. The lengths of these conveyors were: Bridgeport 674 ft., Palmer 612 ft., Gates 150 ft., and Ronco 361 ft. All the conveying equipment for these plants was purchased from the Stephens-Adamson Mfg. Co. All drives, except the Bridgeport which is driven tandem near the tail end, are of the single head-end type. In all cases, the reduction from motor to pulley is through cut steel spur gears. All main bearings are plain, babbitted, grease-cup lubricated. All carriers are Stephens-Adamson ball-bearing Uni-roll type. These ball bearings are of the cup-and-cone type. Each conveyor is fed by an apron conveyor of the corrugated pan type. They started operating in the following order: Bridgeport, March, 1917; Gates, July, 1917; Palmer, July, 1918; and Ronco, October, 1918. At the close of 1924, Bridgeport had carried 4,472,256 tons, Gates 6,211,647 tons, Palmer 4,104,807 tons, and Ronco 6,237,717 tons of coal. All of the conveyors, except the one at Gates, are still operating with the original belts and carriers, and all the belts look good for at least another year's service. The cost records on the carriers show that the upkeep gradually increased up to 1921; since then it has been practically constant. This seems to indicate that these carriers can be kept operating for several years yet at about the present cost. In 1923, we replaced all carriers on the Gates conveyor in order to try a new carrier of the Jeffrey Mfg. Co. In January, 1924, we replaced the belt on this conveyor and used the old belt on the new Colonial system, rather than cut up new belt for the purpose. When taken off the conveyor, this belt was in as good condition as the other belts; showing that if a belt is properly fed about as long a life can be expected from a short one as from a long one.

Very soon after these conveyors were started, it became apparent that they were great labor savers. They carried all the coal that could be hoisted with no delays and were able to handle larger tonnages than they had been designed for. By the latter part of 1919, the output of Ronco mine was brought up to 5000 tons per day, Gates to 3000 tons, and Bridgeport to 2500 tons. The Ronco conveyor handled its tonnage, which was double the amount for which it was designed, with ease and no delays in operation. With the completion of these installations, all the mines owned by the H. C. Frick Coke Co., located directly along the Monongahela River, were equipped to load their entire output in barges for transportation to the Clairton byproduct plant.

Early in 1919, it was decided to increase the capacity of the Clairton byproducts coke plant, when it would require an additional daily supply of 8000 tons. At this time, we had operated river mines long enough to know that a material saving was to be derived by delivering this addi-

tional tonnage by water instead of by rail, so it was decided to transport the coal from the three Colonial mines, lying farther back from the river, to the river and load it in barges. The origin and reasons for the method developed for handling this coal have been described in *Coal Age*, Dec. 25, 1924.

TABLE 1.—*Data Relative to Belt-conveyor Installation for Transporting Run-of-mine Coal from Car Dumper at a Central Point in Colonial Mines 4.3 Miles to Monongahela River*

Belt No.	Size of Belt, Inches	Capacity, Tons	Type of Drive	Length, Feet	Rise or Drop, Feet	Power Required for Starting (Instantaneous) Horsepower	Power Required While Running, Horsepower	Belt Ply	Belt Tension While Running, Pounds	Unit Stress[a]
1	48	1,220	Single	800	− 2.25	248	80	8	8,889	35
2	48	1,220	Single	417	+ 8.1	140	54	8	6,000	31
3	48	1,220	Single	320	+ 4.5	106	39	8	4,334	23
4	48	1,220	Tandem	1,029	+19.6	347	132	8	9,680	38
5	48	1,220	Tandem	1,101	+19.6	369	139	8	10,193	40
6	48	1,220	Tandem	1,497	Level	470	157	10	11,513	40
7	48	1,220	Tandem	1,401	−12.23	425	132	8	9,700	38
8	48	1,220	Tandem	1,500	Level	470	157	10	11,513	40
9	48	1,220	Tandem	933	+11.25	306	111	8	8,140	32
10	48	1,220	Tandem	1,413	+11.2	457	161	10	11,807	42
11	48	1,220	Tandem	1,513	+ 2.72	478	161	10	11,807	42
12	48	1,220	Tandem	1,321	+19.12	438	161	10	11,807	42
13	48	1,220	Tandem	1,324	+23.6	444	167	10	12,247	44
14	48	1,220	Tandem	1,342	+21.07	444	167	10	12,247	44
15	48	1,220	Tandem	1,296	+23.87	444	167	10	12,247	44
16	42	860	Tandem	1,263	+26.3	302	116	8	8,507	34
17	42	860	Tandem	1,366	+17.47	302	116	8	8,507	34
18	42	860	Tandem	1,214	+30.47	302	116	8	8,507	34
19	42	860	Tandem	1,278	+24.97	302	116	8	8,507	34
20	42	860	Tandem	1,212	+30.67	302	116	8	8,507	34

[a] Stress in pounds per inch of width per ply.

These three mines have sufficient acreage of coal to last 25 years, when worked at the rate of 8500 tons per day for 300 days in the year. After a thorough analysis, it was decided to build a system of belt conveyors, having a total length of 22,930 ft., for transporting this coal from a point inside the mine where it was to be delivered in mine wagons.

As soon as this scheme was adopted, we ran a series of power tests on the four conveyors already operating along the Monongahela River, from which we developed a formula that would as nearly as possible fit all when length, speed, load, and lift were taken into consideration.

Knowing the conditions under which these conveyors were operating, this was considered a good basis on which to design conveyors of a much greater efficiency. With these data, lengths of conveyors were established which it was certain could be driven successfully. The data shown in Table 1 were compiled, and from these the entire system was developed step by step. It will be noted that the conveyors were not put in exactly as shown by the original table. Various changes were made to suit local conditions and to take advantage of changes that developed in the scheme as the work of designing proceeded.

The formula used for the preparation of this table was

$$HP = \left(\frac{0.0087L}{100} + \frac{0.01H}{10}\right) \times T$$

This is simply a revision of a formula of Mooney and Darnell,[1] the change being in the percentages of load transferred into motor horsepower. In this formula L is length, in feet, of conveyor, center to center of pulleys; H, lift in feet; and T, tons conveyed per hour.

The result of all the tests on these conveyors showed that we could materially reduce the percentages of load used in the original formula. In the original formula, 2 per cent. of the tons per hour for every 100 ft. of length plus 1 per cent. of the tons per hour for every 10 ft. of vertical lift is used; in the case of these conveyers, this is reduced to 0.87 per cent. of the tons per hour for every 100 ft. of length plus 1 per cent. of the tons per hour for every 10 ft. of vertical lift. These percentages very closely fit the conditions, allowing us to figure back to the actual power consumed on each conveyor. Using this basis for figuring power in establishing lengths, we proceeded to improve the class of equipment for this job as much as possible.

We believe that the power for driving a conveyor is the most important consideration in its design. The actual power consumption, though a considerable item in the operating cost, is the smallest measure of its importance in the design. The power required fixes the size of motor and control, size of main shafts and gear reductions and the ply of the belt, all of which directly affect the installation and overhead costs, and the maintenance and replacement costs.

To reduce power to the minimum, the lubrication of all bearing points must be positive. As each bearing point is also a wearing point, it should be provided with the best possible bearing to suit its condition and also to assure its constant lubrication. All carriers must turn over freely all the time the belt is operating, and as long life as possible be provided. Abrupt bends should be avoided wherever possible, and the coal carried should retain its form as originally placed on the belt by

[1] J. D. Mooney and D. L. Darnell: Conveying Belt Calculating Chart. *Trans.* (1915) **52**, 947.

the feeding arrangement. In case the belt is flattened at any place, the load loses its form and must be forced back to its original shape in going through the next carrier. This requires power, and may readily become a source of increased power consumption. To avoid this, the coal must be carried along in a perfectly quiet state with no changes in its physical form as it lies on the belt.

In the Colonial System, there are in service 6598 carriers, which makes the attendance to bearings and their proper lubrication important. To get the highest possible efficiency every bearing must be in perfect condition and they must always be thoroughly lubricated. By adopting the three-pulley type carrier, the number of bearings and, consequently, the number of places to be lubricated, were reduced from 65,980 to 39,588. The trough of the belt is practically the same as with the standard five-pulley type, making the carrying capacity practically equal to a conveyor equipped with standard five-pulley carriers. It has long been the custom to consider the belt itself as the most important item in a belt conveyor but this is wrong. If the carriers are of a type that can be maintained in good operating condition with all pulleys revolving freely under the load, a much lighter belt can be used on the conveyor, materially reducing the first cost. This reduction in cost is made by reducing the power required to drive the conveyor. If a few of the pulleys become locked and fail to revolve under the load, a great increase in stress is thrown on to the belt and the driving mechanism. A small crusher for crushing coal samples is now being driven from one return carrier; about 3 hp. is required to operate this small crusher, but this power is easily taken off the one return carrier and have it still revolving freely. This shows somewhat the demand for additional power on a conveyor in case one of the return carriers should become locked. The belt in this case slides over the carrier and immediately furnishes the power for driving; this condition is simply exaggerated if some of the troughing carriers under the load become locked. After considering all these features for power reduction, it was decided to adopt either ball or roller bearings of a high class for every bearing point in the system.

As soon as the type of equipment for the system was definitely decided upon, the data shown in Table 2 were prepared. This table shows the characteristics of the various conveyors as they were installed. After these calculations were made, it was found that we were justified in reducing the ply of the belt from 10 ply, over a large part of the system, to 8 ply throughout the system. This reduced the cost of the belt on the entire installation about $50,000, paid for the bearings and more than justified our expectations in regard to reduction in power, as will be shown later.

This conveying system serves three mines, each of which delivers about equal tonnages to the belt. These were all operating mines at the

time the scheme was developed for taking their output to the river, and this change in the operation simply involved increasing the output from an original daily production of about 3350 to 8500 tons per day for the three plants. A point was selected that was as central to these three mines as possible, making their haulages as nearly equal as possible; here a terminal was to be built and the coal transferred from mine wagons to the belt-conveying system. This involved no change in the operation of the mines, with the exception of a reversal of the direction of hauling, and left each of the mines hauling its output about the same distance as when it hauled to its own original opening.

It required better than ordinary provisions to transfer this large coal tonnage from mine wagons to the conveying system. With the mine car in use, it is necessary to dump over 4000 cars per day; since the installation we have actually dumped 5135 cars in one day.

A scheme was developed for using two revolving dumps of sufficient length to handle entire trips of thirty-five cars each. These two dumps are each 374 ft. long, set over a bin of the same length with a capacity of 1250 tons. This gives a storage of one hour between the mine and the conveying system without tying up mine cars. Each of the three mines enters these dumps on its own independent track. The track system is arranged so that Colonial No. 1 and Colonial No. 3 mines, which enter at the same end of the dump, are able to place their trips on either dump by going through a crossover from their own tracks to the parallel, though each normally uses the dump on its own side. The trips from Colonial No. 4 mine enter the dump at the opposite end, using whichever dump is empty. Block signals notify the motormen when each dump is clear.

When a motorman arrives at the dump landing with a loaded trip, he cuts off the locomotive, runs around the trip and pushes it on the dump where it is turned over at once; when righted the empty cars are coupled to the locomotive and returned to the face, with a delay of only a few minutes. By this arrangement, for short periods, loaded trips up to three times the rated capacity of the conveying system can be taken care of as they come in. The bin under the dumps will hold sixteen loaded trips; with the conveyors running this allows a rapid handling, eliminates delays on the haulage system, and keeps all mine cars in motion practically all the time, except when being loaded. One man handles both dumps and takes care of the signals. The dumps are rotated by compressed air, three 17-in. diameter cylinders being used for the overturning and two for the reversing of each dump. Power is applied from these cylinders to the rotating cage structure through long H-beam sections and short lengths of wire rope; this eliminates the unequal stretch of long and short ropes used simultaneously. Ordinarily, not over 5 min. elapse from the time a trip from any mine arrives

at the terminal until it is returning to the working face. These dumps were purchased from the Car Dumper & Equipment Co.

Belt No. 20, which is 60 in. wide, extends under this hopper and is fed by thirty-four apron feeders, which are all in operation at the same time and so designed as to feed a regular tonnage to the belt according to the speed at which they are set to operate. They are all driven by a single variable-speed motor, each feeder being driven from a line shaft that is direct-connected to the driving motor. Chains from this line shaft drive worm-gear reductions, which, in turn, drive each of these feeders. These multiple feeders give a very even load on the conveying system, and, because of the light duty on each, should have a much longer life than could be expected where large tonnage is fed over a single feeder. When the system handles 8500 tons a day, each feeder handles only 250 tons.

Each manufacturer submitting a bid was required to furnish a sample carrier of the type proposed in his proposition. When all these were received and set up in one room, an excellent collection was available from which to choose; they were carefully examined before a selection was made. It became apparent, soon after bids were examined, that to get what was wanted for this system, it would be necessary to consider each item of the equipment separately and purchase each major part of the equipment from the manufacturer giving the best in its line.

The carriers were purchased from the Stephens-Adamson Mfg. Co. This is a three-pulley carrier equipped with No. 204 S. R. B. annular ball bearings. It is substantially made and and all castings are of malleable iron. The bearing housings are of malleable iron, designed with a liberal grease reservoir and mounted so as to oscillate and thus take care of any inaccuracies in alignment—either in manufacture or the result of accidents to the equipment. One unique feature has proved very useful in operation. The entire upper part of the carrier pivots on a fixed shaft, so that it may be turned back under the belt and laid down on the decking, thus permitting each unit to be examined and repaired, if necessary, while the belt is in operation. The return carriers are made of 7-in. tubing with a through live axle and supported at each end on the same bearings in the same mountings as used in the troughing carriers.

After the carriers were selected, it was decided that none of the drives submitted by the manufacturers was satisfactory, so a drive was designed in the company's office and new bids based on this design were obtained.

The motors, which were purchased from the General Electric Co., are of the wound-rotor type, 2300-volt, three-phase, sixty-cycle, 900 r.p.m., the driving pulleys being required to make 40 r.p.m. The motors were to be set in separate drive rooms located back in the coal; it was desirable that all gears be taken out of the main gallery in order to conserve space and remove all possible hazards in operation. A double-

reduction gearbox was designed as a unit to be installed in the motor room between the motor and the tandem driving pulleys. These pulleys were connected to the gear-reduction unit by two extension shafts fitted at each end with flexible couplings of the rubber-bushed pin type to allow for errors in alignment. Cut-steel herringbone gears of small diameter and wide face were used, and all shafts were mounted on high-duty Hyatt bearings. This construction was adopted in order to get the highest possible efficiency from the drives and to allow the entire unit to be made accurately at the factory, assembled, tested, and shipped complete inside the gearbox ready for erection in its room. All gears run in oil, and the roller bearings are equipped so as to be readily accessible for lubrication. The connections between the gearboxes and the motors are made with Falk-Bibby couplings. Seventeen duplicate units of this kind and three of similar construction, but for single drives, were used in this installation. This equipment was purchased from the Falk Corpn.

All drive and head pulleys are 48 in. in diameter, of cast iron, have split hubs, and are mounted on 7½-in. shafts. These shafts are carried by two 6 by 7 in. heavy-duty Hyatt bearings in specially designed ball-and-socket housings. Heavy cast-iron bases are used to mount these bearings. These bases were accurately set to alignment and level, with no provision for adjustment; this worked out nicely, saving time and giving entire satisfaction. All snub and tail pulleys are 36 in. in diameter, with 5½-in. shafts, and are equipped with 5 by 4 in. heavy duty bearings mounted in the same way as the larger ones. The driving pulleys are lagged with four-ply rubber belt. On the tandem drives, the belt is laced underneath first, thus putting the clean side of the belt against the main driving pulley. Each drive has a take-up pulley weighted to apply about 2000 lb. initial tension to the belt. Just ahead of each take-up pulley is a snub pulley, which is provided with a solenoid brake to stop the conveyor and hold it in case there is sufficient lift to cause the conveyor to run backwards after the power is shut off. The Stephens-Adamson Mfg. Co. supplied this equipment.

To provide for lubrication, every bearing in the system was equipped with an Alemite fitting. A car has been built that will carry a barrel of grease and a compressor for forcing the grease through a flexible tube, which is long enough to reach all the bearings. By the use of this car, all equipment can be lubricated at any time desired; this allows fixed periods to be set between complete lubrications of the equipment. Everything is so arranged throughout the system that every bearing can be lubricated with a standard grease gun while the conveyors are running, if this should be necessary.

Carrier spacing was fixed at an average of 3 ft. 6 in., with graduated spacing from the head to the tail end. Various other spaces were

tried on a few conveyors, but no accurate data have been obtained. In the erection of carriers, marks were set on the steel stringers on each side at right angles to the center line of the belt to insure accurate spacing and alignment of carriers. All carriers were clamped to the steel stringers in order to allow of readily changing the spacing.

The belts for this system are eight-ply, 32-oz. duck, $\frac{3}{16}$-in. rubber covered, with the exception of one of the shuttle conveyors, the 60-in. feeding belt, No. 20, under the dumping hopper, and belt No. 19, which are fabric belts manufactured by the Imperial Belting Co. The other belts are divided nearly equally between the B. F. Goodrich Rubber Co. and the Goodyear Tire & Rubber Co.

It was recognized that, on a system as extensive as this, mechanical belt splices would be a serious handicap, so the question of vulcanizing them in the field was discussed with the manufacturers. Three of these units required over 3000 lin. ft. of belt and the average was about 2000 lin. ft. Because of limited headroom in the belt gallery, it was not possible to handle a roll of belting more than 700 ft. long, and most of them were nearer 500 ft. The entire system required a little over 47,000 ft. of belting, making over 100 splices in the entire system. A portable electric vulcanizer was developed, by the Goodyear Tire & Rubber Co., for this job. The vulcanizer was purchased and contracts made with both the Goodyear and Goodrich Rubber companies to make vulcanized field splices on their own belts with this equipment, leaving only one mechanical splice in each belt, which it was proposed to vulcanize after the belts had stretched.

At the end of 1924, 1,265,909 tons of coal had been carried over these belts and none has stretched over 2 or 3 ft., which does not allow enough belt to make a vulcanized splice. In this time, all the original mechanical splices have had to be renewed once, and a few have been renewed the second time. The vulcanizing is well justified, and we are proceeding to vulcanize all of these splices by the addition of a short piece of new belt and a double splice. In making these splices originally, the ends of the belts were stepped down in the factory and vulcanized after the belts were placed on the carriers. This was a successful undertaking and has eliminated much trouble in operation.

The first analysis, Table 1, showed that, with instantaneous starting, the power required to start would be about three times that required for running. As the conveyors used for these determinations were driven by direct-current motors, tests were made of delayed starts by making contacts through a barrel of water and timing the start while measuring the power. From these data it was decided to specify as long a starting duty as possible on the controls to the motors. This was worked out so as to get a 15-sec. starting duty, which reduced the starting power to about twice that for running the loaded belt. This

not only aided in keeping down peaks on the power demand, but materially reduced stresses on the equipment.

The electrical control for a system of belts of this kind required careful consideration. All belts must be interlocked to operate as a unit, and a certain flexibility must be maintained. The control is located in the No. 1 drive room at the river; the operator stationed there controls the entire system and takes calls from the various patrolmen. All units are connected with this room and the office by telephone, and instructions can be issued by telephone from either the office or the control room to any drive room as needed. The operator can start or stop the entire system by pressing a button. On one panel of the board is mounted a voltmeter, which indicates which belts are running and shows where the trouble is located, if anything should stop a conveyor. The control panels are interlocked so that by cutting out resistance at each motor room, as the last accelerating contactor goes in, the reading on the voltmeter is increased to show the conveyor in operation. When conveyors are stopped, this process is reversed.

When the system is to be started, the operator presses the main control button and conveyor No. 1 starts; and as soon as it reaches full speed, or in about 15 sec., No 2 automatically starts; when it attains full speed, No. 3 starts; all conveyors continuing to start in the same manner until the entire system is operating. This manner of starting prevents building up a peak load and allows the entire system to be started without any excess over the regular running load, with the exception of the extra starting load on the last conveyor. The equipment is so interlocked that if any motor is shut down every conveyor back of it is instantly stopped. This stop may be caused automatically by a line contactor of any starter opening because of overload, by the breaking of a conveyor belt, or by a belt slipping on one of the driving units more than a predetermined amount. In case of power failure, all motors will stop and will not start again until started from the main control room.

Each conveyor is provided with a limit switch operated from the idler pulley of the belt take-up, so that if the belt stretches beyond a certain point or breaks, the motor will be shut down, together with all motors back of it. An emergency switch is located in the belt gallery near each motor room, which, if opened, automatically stops all motors; all these switches must be closed before the accelerating equipment will be operative. Each starting panel is provided with a switch by which it may be disconnected from the master control system and operated as a unit if required in case of testing, splicing a belt, or any other cause requiring such operation.

When making a stop the belts will naturally coast varying distances, because of the difference in lengths and lifts. While solenoid brakes are provided on each conveyor, it was not considered advisable to set them

so that they would engage hard enough to bring the belts to an immediate stop. To prevent a free-running conveyor from discharging coal upon one ahead that had stopped, a mechanical interlock was installed between the head and tail pulleys of each conveyor on the system. This engages whenever the conveyor at the rear tends to run faster than the one ahead of it and prevents any piling up of coal in the chutes. As all these safeguards are working satisfactorily, we have never had any trouble with these conveyors.

The designing of the chutes between conveyors gave much trouble, as the headroom has to be kept to a minimum. The large lumps sometimes clogged the chutes a little as originally designed, but this was easily corrected by cutting a V-shaped notch at the bottom. The chutes now load the conveyors uniformly throughout the entire system.

At the river, or discharge, end of this conveying system, a large river tipple was built. The coal, when discharged from No. 1 belt, passes over a long bar screen with bars spaced to pass coal of a desired size. All small coal is collected in a chute that feeds a shuttle conveyor, distributing it uniformly over the entire length of a slack-coal bunker. The coal passing over this screen is fed to a duplicate shuttle conveyor, which distributes it over the lump-coal bunker. These shuttle conveyors are manually or automatically operated, as desired, and so interlocked with the main system as to start with the other belts, thus preventing any flooding of coal at the start. Each has a capacity of 1000 tons per hr., allowing for variations in the quantity of slack in the coal, such as at times will occur.

The bunkers are of the suspended type, being suspended over the river from heavy girders resting upon six large concrete piers. Each bunker has a capacity of about 1200 tons. Coal is taken from the bottom of the bunkers through eight gates spaced so as to feed coal uniformly to a barge 175 ft. long. This allows each barge to be completely loaded without moving. A barge of 850 tons capacity can easily be loaded in 10 min. The chutes leading from the gates to the barge are arranged to telescope to allow for varying heights of water in the river.

The gates and telescoping chutes are operated by electric motors, which are centrally controlled in a cabin located beneath the bin, whence the operator has a clear view of all operations. The gates are opened by torque motors, which hold them open as long as the electric current is kept on them. They are counterweighted, so as to close automatically as soon as the current is cut off; in case of power failure, the gates immediately close. The operator can open or close all gates at once, or any individual gate or number of gates, by simply pressing the proper buttons on his board. A small barge mover for handling both empty and loaded barges is also operated from this same board. A large reinforced-

TABLE 2.—*Conveyor Data*

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18		19	20	21	22
Belt No.	Length, Feet	Net Rise or Drop, Feet	Est. Wt. Running Parts Empty, Tons	Est. Wt. Coal at 1220 Ton-Hr., Tons	Est. Wt. Running Parts Loaded, Tons	Tension Load Carried by Pulley Bearings, Tons	Power Requirements of Empty Conveyor, Horsepower	Power Requirements to Raise Live Load, Horsepower	Running Power Requirements without Lift, Horsepower	Total Running Power Requirements, Horsepower	Horsepower of Electric Motor	Start Power Requirements Empty 15 Sec., Horsepower	Start Power Requirements Loaded 15 Sec., Horsepower	Initial Tension, Pounds	Belt Tension Running, Pounds	Belt Tension Start 15 Sec. Loaded, Pounds	Est. Travel of Loaded Belt to Stop		Lineal Feet of Belt Required, Net	Number of Carriers Required	Number of Return Rollers	Belt No.
																	Ft.	Ft.				
1	786	43.42	37	31	68	17	11	+60	51	111	150	70	200	1,500	8,050	13,350	23	35	1,636-6	225	78	1
2	417	8.30	20	17	37	9	17	+12	28	40	50	39	87	2,000	4,320	7,210	35	82	867-6	120	41	2
3	321	4.85	17	13	30	9	5	+ 7	23	30	50	32	69	1,500	3,240	5,580	38	88	675-6	92	32	3
4	1,029	19.88	45	41	86	19	15	+27	65	92	125	87	204	1,500	6,950	13,660	35	73	2,113-6	294	102	4
4	1,101	21.07	47	44	91	20	16	+29	69	98	125	91	217	1,500	7,290	14,390	35	73	2,258-0	315	110	5
6	1,496	4.20	60	60	120	24	21	+ 6	91	97	150	117	234	2,000	7,740	17,100	46	156	3,047-6	428	149	6
7	1,402	−12.23	57	56	113	24	20	−17	114	97	150	111	245	2,000	7,800	16,610	43	349	2,858-0	401	140	7
8	1,500	1.47	60	60	120	25	21	+ 2	91	93	150	117	250	2,000	7,540	16,900	48	179	3,055-6	429	150	8
9	938	11.09	42	37	79	18	14	+15	59	74	100	81	176	1,500	5,840	12,000	40	102	1,931-0	268	93	9
10	1,410	12.33	57	57	114	23	20	+17	86	103	150	111	254	2,000	8,220	17,110	40	105	2,875-0	403	140	10
11	1,514	3.26	61	60	121	25	22	+ 5	92	97	150	120	255	2,000	7,710	17,150	47	164	3,082-0	433	150	11
12	1,320	29.64	54	53	107	23	19	+40	81	121	175	105	262	2,000	9,230	17,580	32	65	2,695-0	378	131	12
13	1,326	22.89	55	53	108	22	19	+31	81	112	175	107	254	2,000	8,690	17,110	35	77	2,707-0	380	132	13
14	1,342	24.42	55	54	109	22	19	+33	82	115	175	107	258	2,000	8,870	17,370	35	74	2,740-0	384	134	14
15	1,296	25.36	54	52	106	22	18	+35	80	115	175	104	253	2,000	8,810	17,080	34	72	2,648-0	371	129	15
16	1,263	27.92	53	50	103	21	18	+38	77	115	175	103	250	2,000	8,850	16,880	33	66	2,582-0	361	126	16
17	1,366	19.12	56	55	111	23	19	+26	84	110	175	109	255	2,000	8,540	17,200	37	87	2,788-0	391	136	17
18	1,301	34.04	54	52	106	22	18	+46	80	126	175	104	265	2,000	9,510	17,780	31	59	2,659-0	372	130	18
19	1,244	36.19	52	50	102	21	18	+49	77	126	175	101	260	2,000	9,500	17,460	30	55	2,542-0	356	124	19
20	558	20.20	31	34	65	10	11	+27	34	61	100	35	103	3,000	8,250	11,820	14	23	1,151-0	197	54	20
21 &	60 Cts.										1-15 & 1-5								134-0			
22											to each								134-0			
Tot.	22,930	357.42								1933									47,080-0	6,598		

TABLE 3.—*Actual Test Data after the Installation*

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
												Level Belt Demand Measured as Additional Power Above Empty Demand Column 11 less 12		Constant Kw. per 100 Tons per 100 Ft. Based on Column 13.			
Belt No.	Length, Feet	Lift, Feet	Date of Test	Tons Carried for Day	Total Kw.-hr. for Day	Time that Belt Ran, Minutes	Time that Belt Carried Load, Minutes	Average Load, Tons per Hour	Demand for Empty Belt, Kilowatts	Added Kilowatts Above Empty Demand to Carry Average Load	Kilowatts to Lift Load, Average	Kw.	Hp.	Kw. 100T/100 Ft.	Hp. 100T/100 Ft.	Kw. per 100 ft. of Conveyor Empty Belt	Belt No.
1	786	43.4	8- 4-24	6,346	460	368	352	1,080	19.2	51.6	39.8	11.8	14.2	0.139	0.167	2.44	1
2	417	8.3	8- 5-24	6,418	174	360	327	1,180	12.8	14.1	8.3	5.8	7.0	0.118	0.142	3.35	2
3	321	4.8	8- 7-24	6,460	144	350	326	1,192	12.8	9.3	4.9	4.4	5.3	0.115	0.138	4.00	3
4	1,028	19.9	8-11-24	6,500	410	395	350	1,115	24.0	35.0	18.9	16.1	19.3	0.140	0.168	2.33	4
5	1,101	21.1	8-12-24	6,854	420	390	333	1,235	27.0	36.7	22.2	14.5	17.5	0.105	0.128	2.45	5
6	1,496	4.2	8-14-24	7,122	410	370	350	1,222	31.1	29.0	4.4	24.6	29.5	0.134	0.178	2.09	6
7	1,402	−12.2	8-15-24	6,884	330	395	389	1,060	28.8	17.5	−11.0	28.5	35.2	0.192	0.230	2.05	7
8	1,499	1.5	8-16-24	6,750	400	415	361	1,120	28.8	27.9	1.4	26.5	31.8	0.158	0.189	1.92	8
9	939	11.1	8-19-24	7,032	358	376	361	1,142	25.6	26.0	10.8	15.2	18.2	0.142	0.170	2.73	9
10	1,410	12.3	8-21-24	7,833	440	389	354	1,336	24.0	37.0	14.0	23.0	27.6	0.122	0.147	1.70	10
11	1,513	3.3	8-23-24	7,250	400	388	359	1,212	28.8	30.2	3.3	26.9	32.2	0.146	0.176	1.90	11
12	1,321	29.6	8-25-24	7,271	530	375	340	1,282	32.0	52.0	32.3	19.7	23.6	0.116	0.139	2.42	12
13	1,325	22.9	8-26-24	7,252	480	374	342	1,272	26.5	47.2	24.8	22.4	26.9	0.132	0.159	2.00	13
14	1,342	24.4	8-28-24	7,085	490	377	345	1,232	26.0	49.0	25.6	23.4	28.0	0.141	0.169	1.94	14
15	1,296	25.4	8-29-24	7,341	500	367	334	1,320	24.0	49.9	28.5	21.4	25.7	0.125	0.150	1.85	15
16	1,263	27.9	8-30-24	7,939	430	400	350	1,362	26.4	50.1	32.3	17.8	21.4	0.103	0.124	2.09	16
17	1,366	19.1	9- 1-24	6,225	440	355	340	1,100	26.0	42.0	17.9	24.1	28.9	0.160	0.192	1.90	17
18	1,301	34.0	9- 2-24	7,235	520	370	363	1,196	24.0	53.3	34.6	18.7	22.5	0.120	0.144	1.84	18
19	1,243	36.0	9- 4-24	7,847	650	375	353	1,334	28.8	71.7	40.8	30.9	37.1	0.186	0.223	2.32	19
20	558	20.7	9- 5-24	7,421	307	440	283	1,575	12.8	48.7	27.8	20.9	25.1	0.238	0.285	2.30	20

concrete ice breaker protects this harbor, in which space is provided for storing ten empty and ten loaded barges.

The conveying system was started in regular operation on April 12, 1924, and at the end of January, 1925, had carried 1,512,741 tons. The largest day's production was 10,589 tons. During January, this system carried 246,832 tons of coal, or an average of 9142 tons per day for 27 operating days. With these results, we feel safe in stating that this system will handle 3,000,000 tons during 1925, if business conditions will allow it to be operated regularly at the best rate that can be maintained. The power requirements for January were 0.349 kw. per 100 tons per 100 ft. level or equivalent. The total power used for operating the conveying system, pumps, fan, and for charging storage-batteries, including transformer and line losses, was 380,000 kw.-hr., of which 285,660 kw-hr. was required for the conveying system.

In August and September, power tests were run on all the conveyor units. Each test was for an entire day, and accurate power readings were taken, the time the belt operated loaded and empty and the tonnage handled were recorded. The data shown by Table 3 are the result of this series of tests. At the time they were made, the tonnage was less than is now being carried, but the results should be fairly representative of the power consumption.

From these data, a formula has been prepared for calculating the horsepower required to drive conveyors completely equipped with anti-friction bearings of the class being used. This formula applies only to 48-in. belt conveyors of long centers. It is divided into three parts, the power to drive a belt conveyor empty, plus the power to carry a given tonnage a horizontal distance, plus the power to lift this tonnage a given height.

The first part, or empty-belt power, is one of friction, both rolling and bearing, and is not exactly proportional to length because the loads and belt stresses carried by main bearings are practically constant regardless of length, whereas the carrier rims and belt weight are directly proportional to length. We find from these tests that lift has practically no influence on the power used by a belt conveyor running empty. On such conveyors as are used in this system, the lengths and conditions are so nearly constant that the power per 100 ft. of conveyor is almost uniform, and in this formula we have taken the constant K which represents the power per 100 ft. of conveyor directly from the data as tabulated. This constant presupposes that all parts of the equipment are in first-class condition. Its average value on all conveyors in the system having tandem drives is 2.11 kw. or about 2.5 hp. For safely estimating power, the value recommended is $K = 2.8$, when figuring the horsepower of conveyors of this class. The power for an empty conveyor where K = constant representing conditions and class of equipment,

and L = length of conveyor, in feet, between centers of head and tail pulleys is given by:

$$\text{Empty power} = \frac{KL}{100}$$

The second part of this formula represents the resistance of the live load added to the empty belt, which is simply bearing friction and rolling friction of this additional load on the carriers. This part of the power is directly proportional to the length of conveyor and the tonnage carried and can be expressed as follows:

$$\text{Power for live load} \quad \frac{CTL}{100 \times 100}$$

Where C = constant power required to carry 100 tons 100 ft., T = tons per hour, and L = length of conveyor in feet.

The last part of the formula takes into consideration the direct work of raising this load a given height with an allowance for electrical and mechanical efficiency. This can be expressed as follows where H = height of lift, in feet and D = constant due to efficiency:

$$\text{Power for lift} = \frac{DTH}{1000}$$

Assembling these various components we have, for driving conveyors of long centers with tandem drives with all bearings of high-class anti-friction type

$$\text{Horsepower} = \frac{KL}{100} + \frac{CTL}{10{,}000} + \frac{DTH}{1000}$$

For conveyors of this class, the value of the constants for figuring horsepower of conveyors is as follows: $K = 2.8$; $C = 0.18$, and $D = 1.12$.

After running tests on all conveyors of the system and carefully analyzing the results, we found that a further saving in operation could be made by combining conveyors Nos. 8 and 9, making a single conveyor 2439 ft. long and driven by the motor that originally drove No 8. These two conveyors were in a straight line and by combining them we could reduce the lift by 4.1 ft. On Saturday afternoon, Jan. 24, we started making the necessary changes to combine these units into one conveyor and the work was completed and the belt trained Sunday evening. The new conveyor was started in operation on Monday morning, Jan. 26. A test for an entire day's run, the same as made previously on the other conveyors, was run on this conveyor on Jan. 28, with the following results:

Tons carried for the day	8866
Time belt operated, minutes	473
Time belt carried load, minutes	460
Average load, tons per hour	1156
Power demand for empty belt, kilowatts	36.0
Additional demand to carry average load, kilowatts	51.7
Power required to lift load, average, kilowatts	8.1
Level belt power demand measured as additional power above empty demand (Column 11 less Column 12), kilowatts	43.6
Constant power required per 100 tons per 100 ft., based on Column 13, kilowatts	0.155
Kilowatts required per 100 ft. with conveyor empty belt	1.47

This test shows that by connecting these belts we have made a saving of 4446 kw.-hr. per month, or approximately a 20 per cent. power saving. The saving is primarily in the empty power, except that accounted for by eliminating 4.1 ft. of lift. The power to carry a load, deducting lift and empty power, checks almost exactly, which we expected, indicating this to be friction and directly proportional to the weight of material. The maximum starting duty of this conveyor, measured as relative torque, is 240 hp. in 20 sec., with a load on the belt of 1340 tons per hour. This gives a maximum belt stress of 16,200 lb., or 42.2 lb. per in. per ply on starting duty. The running stress is 9200 lb., or 24.2 lb. per in. per ply.

While this consolidation of two conveyors into one makes a very long unit, in all cases the final power figure is less for the long conveyor than the combined powers for the two, and the belt stress on starting is still lower than what was originally figured for conveyor No 8 alone, with the running stresses less than conveyor No 11 was originally figured. This change eliminates one drive completely, making a motor and complete driving unit available for use at some other place and eliminates the upkeep on one transfer point.

We have not given operating figures on this system, mainly for the reason that any such figures taken at this time would be misleading. It will take a few years' operation before any figures can be derived that would be safe for general use.

In closing, we would state that the operation of these conveyors proves conclusively that a belt conveyor is dependable in its operation; positive in its performance; durable to an extent greater than most machines; less hazardous to life and not entirely dependent on the human element. In handling over 1½ million tons of coal, there has not been a single accident to a man on this operation. A result of this kind would have been almost impossible if this amount of coal were hauled by electric locomotives over this distance. The conveyors require few men to operate, are not excessive in first cost, and have low operating charges.

DISCUSSION

F. F. Jorgensen, Gillespie, Ill.—What was the cost of that conveying system and what is the cost per ton of conveying?

Thomas W. Dawson.—I cannot give the cost of the conveying of the coal, but I assure you it is quite low; the cost of the system is about $2,500,000.

F. F. Jorgensen.—Why was it made in three sections instead of the ordinary five?

Thomas W. Dawson.—The principal reason was to reduce the number of bearings.

F. F. Jorgensen.—Won't there be a tendency for the belt to slip?

Thos. W. Dawson.—I see no difficulty.

Graham Bright, East Pittsburgh, Pa.—Were the figures for January for total tonnage?

Thomas W. Dawson.—The total tonnage for the month of January was 226,832 tons of coal and the power requirements for that month were 0.349 kw. per 100 tons for 100 ft. For operating the entire system, including the pumps and fan, charging of storage battery motors, a total of 38,000 kw.-hr. was required and 285,660 kw.-hr. was used in the conveyor system.

Graham Bright.—Did that include all of the main haulage from the inside gathering points to the river?

Thomas W. Dawson.—Just from the dump to the river. We are also pumping water and ventilating the system and we do some lighting.

Graham Bright.—The paper stated that 500 ft. was the maximum length of belt on account of the size of roll. Would it not be possible to feed the belt in from one end, and after the first belt is put in operation, use this belt as a carrier for, the second belt, which would enable the use of longer lengths and less splicing?

Thomas W. Dawson.—That plan was considered but we decided to take the sure method. We might do it by reversing the belt, but in different parts of the system certain parts were prepared before other parts, so we used shorter units to facilitate the work. We had a special car made for rolling the belt in about 500-ft. lengths. We have had no trouble whatever in handling it.

Graham Bright.—If you were going to do it over again would you use longer belts?

THOMAS W. DAWSON.—Yes; even on our first installation we went beyond the belt lengths, from center to center, recommended by various manufacturers. In another installation we would have them longer.

A. W. HESSE.—How much time was required for the installation of this system?

THOMAS W. DAWSON.—From the time we started it was just about 3 years but the greater part of the time was spent over that 4.3 miles of heading from the river to the dump, putting in the steel supports for continuity of surface. The belt conveyor could be installed in a year; the preparation of heading took the time.

When we first thought of transporting coal underground to the river, we purchased from the Pittsburgh Coal Co. two headings in an old mine 2½ miles from the river to the boundary line together with sufficient support on either side, or about 100 acres of coal. That mine was probably opened 45 or 47 years ago. The first 2000 ft. from the river is on cribs and we could not get to either side of the open headings. It just had the appearance of being gobbed out to the headings.

Review of Coal-dust Investigations

By George S. Rice,* Washington, D. C.

(New York Meeting, February, 1925)

Ten years ago, October, 1914, the author had the privilege of giving an illustrated address on investigations of coal-dust explosions[1] to this Institute at one session of its fall meeting in Pittsburgh, Pa. On the following day, the members had the opportunity of seeing a large-scale explosion test at the Experimental Mine near Bruceton, in which the explosion was made to follow a predetermined path by means of rock-dust barriers of various types, which had prevented the explosive waves from reaching the outlets of the mine by the shortest paths.[2] There was also shown a "home-made" rock-dusting machine discharging the dust from a flexible nozzle, and a cement gun operated for the quick erection of a fire or ventilation stopping, such as might be put up after an explosion.

Following that paper, there was presented a paper by J. Taffanel, Director of the Liévin testing station in the Pas de Calais, which reviewed the French coal-dust investigations.[3] A paper[4] by Howard N. Eavenson contains lists of explosions that occurred in North America and Great Britain, from early in the 19th century to 1912; in France to 1903, and Belgium to 1909. Although explosions still occur, we are hopeful that we have entered a happier freedom from these visitations, as the result of increased knowledge of the causes and means of prevention. Looking back over coal-dust investigations, there appear to have been periods of advance and of stagnation.

Coal-dust Investigations

From the earliest times of coal mining, which chiefly affected Great Britain as the first nation to take up coal mining on a large scale, to the beginning of the 19th century, no one thought of coal dust as an explosive agency; firedamp was the cause dreaded.

It was believed, when Sir Humphrey Davy invented his safety lamp in 1815, that a solution had been found for the prevention of mine explo-

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* Chief Mining Engineer, Bureau of Mines.

[1] *Trans.* (1915) **50**, 552.

[2] Diagram of this explosion and its results, which was witnessed by many members of the Institute, coal operators, and representatives of several state inspection departments, are appended to this paper, together with a brief explanation.

[3] *Trans.* (1915) **50**, 588.

[4] Coal-Mine Explosions Caused by Gas or Dust. *Trans.* (1915) 50, 594.

sions. Nevertheless, the use of the safety lamps was not universal and the primitive forms were imperfect. Also, mine ventilation was extremely crude. As explosions continued to occur, firedamp was naturally regarded as the great danger, for coal dust was not known to be a factor.

In 1803, in connection with the Wall's End (Newcastle-on-Tyne) mine explosion the first suggestion was recorded that coal dust may have been a factor. Between this time and 1860, mention was made from time to time, following explosions in France and Great Britain, that coal dust was a factor in firedamp explosions, notably by Faraday and Lyell (1845), and du Souich of France (1855). The earlier mention related to its effect in burning men by the clots of flaming dust; the later suggestions were that it played a part by extending the flame of an explosion. Faraday suggested, in his report on the Haswell Colliery explosion, that firedamp was not the only fuel and that much coal gas was raised from the dust which had been coked.

The decade 1861–1870 was marked by two explosion disasters in Great Britain: Oaks colliery, Yorkshire, 1866, with 361 deaths; Ferndale, Wales, 1867, with 178 deaths, followed 18 months later, in the same colliery, by another explosion costing 53 deaths. There were 33 explosions each costing over 10 lives, and there was a total death roll from these explosions of 1444.

In France, during this decade, there were six disasters, each causing ten or more deaths; one of these cost 89 lives. From 1864 to 1867, Verpellieux in France made the first experiments on coal dust inflammability that the author has found recorded. He concluded that coal dust was a most important factor in mine explosions and likened it to firing a gun with ammunition of that day, in which firedamp was the primer and coal dust the powder.

During the decade 1871–1880, 35 explosions costing 2014 lives occurred in Great Britain. The most severe was at Abercarne, Wales, with 268 deaths. In France, the Jabin colliery had an explosion, in 1871, that cost 70 lives and another in 1876 that cost 186 lives.

Laboratory and Small-gallery Testing

It was during this decade that laboratory investigations were taken up actively. Vital, in France in 1875, made an apparatus with which he attempted to obtain the pressures produced by an ignition of different dusts. He was the first to conclude, on the basis of experimentation, that dusts rich in gas might ignite directly from a blown-out shot. Apparently he was much "ahead of his time" in France. In December, 1875, Galloway began his laboratory experiments (reported to the Royal Society, London, 1876) which led him to the conclusion that a small percentage of firedamp must be present to obtain propagation. Although

he suggests that if coal dust were made fine enough and were thoroughly mixed with air, it might propagate an explosion. Galloway, however, did not come out until 10 years later with a direct statement that coal dust would propagate an explosion without firedamp being present.

At this time (December, 1875) Marreco began some small-gallery tests at Elswick colliery and decided that coal dust would propagate an explosion without firedamp.

Large-scale Testing by Henry Hall

Hall, in 1876, made the first recorded large-scale tests in a short mine adit, and concluded that coal dust alone would carry the inflammation of a blown-out shot. In referring to the experiments, the Royal Commission expressed suspicion that there might have been firedamp present.

Abel's Small-gallery Tests

In 1880, following the Seaham explosion, Sir Frederick Abel, an explosives expert and a member of a Royal Commission on Accidents in Mines, undertook small-gallery tests and reached the conclusion that although coal dust was an important factor, firedamp must be present. Abel's conclusions, through his prominence, caused a decided setback for some years of the opinion that coal dust was a sole agent.

It is now evident that the laboratory and gallery testing of that day was very crude, being conducted with no knowledge of the character of the dust tested, its volatile-fixed carbon ratio, purity, and size of dust particles. Such crude methods of testing, both in the laboratory and large-scale testing, continued for nearly 30 years and the inconsistent results befogged the question of coal-dust explosibility.

1881–1890

This decade witnessed important developments in coal-dust investigations, although the battle was still waged, as stated by a Frenchman, between the coal dust and the anti-coal dust adherents.

British Views

British mining engineers and operators at the beginning of the decade were skeptical but, by 1886, many had accepted the theory that coal dust was a serious hazard, whether or not it was explosive alone in air. The Royal Commission report of 1886 also took this position but mentioned that a highly inflammable coal dust in great abundance might, in the absence of firedamp, be ignited by a blown-out shot.

Galloway strongly advocated watering roadways, which originally had been done in some mines as a hygienic measure, but there was much opposition, from the majority of the mining men of England, to general

watering on account of the damage to the naturally dry and friable roof and floor.

Watering and the use of compressed-air sprays were introduced in some of the Welsh mines. The Mines Act of 1887 called for watering before shot-firing in a "dry and dusty place," for a distance of 20 yd. from the shot.

In this decade, there was a larger use of safety lamps and general precautions in preventing ignition of firedamp, which probably was helpful in reducing explosion disasters in British mines to 26 and deaths to 1292.

French Anti-coal-dust Explosibility Conclusions

In 1882, the distinguished French scientists, Mallard and Le Chatelier, after studying mine-explosion evidence and making tests of coal dust in conjunction with more or less firedamp, concluded that it was necessary that firedamp be present with coal dust to obtain explosibility of the latter and therefore if firedamp was well removed from the mine by ventilation, there was little danger from the coal dust. At that time, and even after the Courrières disaster in 1906, it was common practice, in getting coal from workings, to shovel or dump the coal down vertical winzes or steep chutes to a haulage level below, thus making clouds of dust in the vicinity.

Although a great explosion occurred in the Verpellieux colliery in 1889, taking 207 lives, and one in the Pilisnier colliery in 1890, killing 113, the view of Mallard and Le Chatelier had a most important influence in preventing recognition of the coal-dust hazard until after the Courrières disaster. Meantime, the French mines were taking the greatest care as regards firedamp, and certain mines in the Pas-de-Calais-Nord district were the first to sample and analyze the air of the mine systematically each day.

German Gallery Testing

In Germany, the Prussian Firedamp Commission began, in 1884, to experiment with coal dust and coal dust and gas in a surface gallery 167 ft. long, in the Saar. Its conclusions are not very definite on the question of coal dust being an explosive agent in air only, but it compromised by saying that coal dust of certain descriptions may propagate flame of a blown-out shot even beyond the limits of the dust deposits.

The Austrian Mine Explosion Commission, which began testing in a gallery in 1886, reached conclusions that coal dust was dangerous and could be ignited by 100 gm. of dynamite but did not affirm that it would propagate an explosion to indefinite limits.

United States Mine Explosions Prior to 1881

The United States, during the decades previous to 1881, had comparatively few major explosion disasters, the exceptions being four disasters in

the limited but gaseous Richmond, Va., basin. The production of bituminous coal in the entire United States in 1880 had reached only 43,000,000 tons and much of this was mined by undercutting with picks. The bituminous production of the country rapidly increased after 1880 and, by 1890, had reached 111,000,000 tons or two and one-half times as much as in 1880. This increase was accompanied by the occurrence of large explosions from 1881 to 1884, inclusive, when there were seven explosions, costing over 10 lives each. The explosion at the Pocahontas Mine, Virginia, which caused 114 fatalities, was attributed, by the committee appointed by this Institute, to "dust alone or dust quickened by an admixture of firedamp too slight for detection."[5]

W. N. and J. B. Atkinson issued, in 1886, their publication on Explosions in Coal Mines; they designated coal dust as the principal factor in a group of explosions they had investigated, and in certain explosions as the sole factor.

Garforth's Observations of Altofts Mine Explosion Regarding Stone Dust

In 1887, the now famous Altofts mine explosion occurred, and the observation then made by William Garforth during the investigation led him later to propose a new method of coal-dust explosion prevention—stone dusting. The explosion did not claim a large number of victims, only 22, but the coroner's verdict placed the cause wholly on coal dust. This was the first time, at least in Great Britain, that such a verdict had been rendered. Mr. Garforth (later Sir William Garforth), the agent and general manager, noted that the explosion had not penetrated any of the naturally shale-dusted passages. This fact led later to suggestions, reported in the evidence given to the Royal Commission on Coal Dust in Mines, July 2, 1891, that experiments should be made on different kinds of coal dust and "dirt" dust. "I believe dirt dust will really be the means of preventing an explosion in certain roads more so than watering." Other persons had commented, among them the author,[6] that natural admixing of shale and clay with coal dust prevented propagation but here is a suggestion for the first time, so far as the author can find, of introducing into the mine road inert material to neutralize the explosibility of coal dust.

1891–1900

British Mine Explosions

In Great Britain, this decade marked a great reduction of disastrous explosions. Only 10 occurred in which 10 or more men were killed, including the great disaster at Albion, Wales, costing 290 lives. The

[5] *Trans.* (1885) **13**, 237.

[6] Pekay (Iowa) Mine Explosion. *Jnl.* Illinois Min. Inst. (1893) **2**, **54**.

total loss for the decade, is only 733 lives, which is 43 per cent. less than in the previous decade. This reduction, in part, was probably due to good fortune but chiefly to improvements that lessened the liability of igniting methane and coal dust; so-called flameless or safety explosives, first developed in Germany and France, began to be used in Great Britain at the beginning of the decade. In 1897, the British Government installed gas and coal-dust galleries or tubes for testing mining explosives at the Woolwich Arsenal.

The British Commission on Coal Dust sat from 1891 to 1894. Galloway gave testimony, in 1891, indicating that he was strongly of the opinion that coal dust in air only was capable of carrying on an explosion. Explosibility varied with fineness of dust and had no connection with chemical composition and he thought that the finest dust from all kinds of coal, except anthracite, was explosive. We now know that relative explosibility depends on the volatile combustible ratio, the noncombustible present, as well as the fineness. Also, with natural coal mine dusts, it is probable that the structure of the particles is a factor in relative inflammability or ease of ignition.

Safety Explosives Approval, Germany and France

In Germany, explosives-testing apparatus, of a kind still used, had been developed by explosives manufacturers. In 1894, a gallery for testing explosives in gas and dust was established by the mine operators at Gelsenkirchen. The Prussian Firedamp Commission, as a result of further testing, declared that black powder, other slow explosives, and also dynamite, should not be used in the presence of firedamp when there was enough to make a clearly perceptible "cap" in a safety lamp, which would mean 1 to 2 per cent., depending on the lamp used.

The French, after numerous laboratory tests, decided that no explosive should be used in a gaseous mine, when the calculated temperature of the explosives, in exploding, exceeded 1500° C., which temperature they considered would prevent the ignition of firedamp. In this decade (1890–1900) they were still acting on the conclusions of Mallard and Le Chatelier, that coal dust was unimportant if precaution was taken against firedamp.

Mine Explosions in the United States

In the United States, during this decade 18 explosions costing 10 or more lives each, occurred in the bituminous mines, but there was only one great disaster attributable to coal dust, that of Scofield, Utah (May 1, 1900), with 200 deaths. Watering the dusts was increasingly practiced but not enough to be an important factor. During this period (in 1897), in the Middle West, a change was made by labor agreements and, in some States, by legal enactment, under which a miner was no longer

paid on the amount of lump coal he produced, but on the basis of the run-of-mine he loaded. This led to the excessive use of explosives and "shooting off the solid" which resulted in so many explosions, most of them fortunately limited in fatalities, that the system was introduced of shot-firing when all persons except the shot-firers were out of the mine. Thus, while there were just as many explosions, some of them widespread and causing property destruction, only the shot-firers were killed. In the Indian Territory (Oklahoma) alone, between November, 1893, and the end of the decade there were recorded 22 shot-firers' explosions with 33 fatalities, although the district then produced less than 2,000,000 tons of coal per annum.

1901–1910

United States Mine Explosions

This is the most important decade as concerns coal dust, although in the first half there were no unusual happenings. In the United States, shot-firers' deaths continued to occur with an alarming frequency. As regards major disasters, there were 22 explosions killing over 10 men each, from 1901 to 1905, inclusive. The larger explosions were Coal Creek, Tenn. (184); Rolling Mill, Pa. (112); Hanna, Wyo. (169); Harwick, Pa. (178); and Virginia City, Ala. (111). Watering methods were more extensively used in this period to reduce coal dust, and some use of the so-called safety explosives of German type was made.

British Requirement of Permitted Explosives

Great Britain, in 1896, had enacted a regulation that any explosive likely to be dangerous might be prohibited for use in mines and later began testing explosives at Woolwich. In 1902, it followed the practice of Belgium, Germany, and France, and adopted an approval system for explosives used in gaseous and dusty mines, and issued a "permitted" list. This list was modified from time to time as the test requirements were increased.

The explosion disasters in Great Britain, between 1901 and 1905, were relatively few—5 occurred costing 10 or more lives, with a total of 260 deaths.

French and Belgium Mine Explosions

France had few disasters in the first five years; Belgium, as usual, had few. Belgian mines are very gaseous but the coal-dust problem away from the face has been inconsequential; there is so much natural mixing of shale dust and clay. The greatest care was taken to avoid accumulations of coal dust, only officially approved explosives were used, and watering down in the vicinity of a shot was done before firing.

Germany

Germany employed watering extensively at this period. Its deep hot mines were very humid and the hookworm became a menace until hygienic remedies were found. Nevertheless serious explosions occurred from time to time.

Courrières Mine Explosion, France

The second five years, 1906 to 1910, opened with the most serious mine disaster in history, the Courrières explosion, in France, which occurred March 10, 1906, killing 1100 men in what was rated a non-gaseous mine. Unquestionably from the evidence gathered it was due to a coal-dust explosion, the dust being ignited by a blown-out shot.

Liévin, France, Testing Station Establishment

This disaster immediately led the Central Committee of Coal Operators of France to establish a coal-dust explosion station with gallery at Liévin, in charge of a Government mining engineer, J. Taffanel. He employed more carefully controlled testing methods than had been done hitherto in gallery experiments. The first gallery was a small one arranged in an ellipse to give a closed circuit for air currents until certain paper diaphragms were ruptured by a shot. Prior to firing the shot, the air and dust were stirred and circled around by a disk fan. Taffanel studied the relative explosibility of prepared dust from different mines, by comparison of the lowest density of the dust in air, which could be ignited. He reported the result in August, 1907. He found the explosibility varied with the volatile combustible content of the dust. Meantime, the construction of a large gallery was begun, 30 sq. ft. in cross-section; in 1909 it was completed to a length of 750 ft., and ultimately to a length of 1000 ft. Taffanel began, in 1910, issuing his series of reports on the testing in the gallery.

Altofts (England) Coal-dust Gallery Establishment

British mining men were greatly disturbed by the Courrières disaster; the Government sent a commission to France to investigate it. A Royal Commission was appointed June, 1906, on questions relating to the health and safety of miners. The evidence on the coal-dust question continued to be conflicting so the Commission appointed a committee to report what further experiments were necessary. The committee reported, April 30, 1907, that large-scale experiments were necessary and recommended a gallery of the same diameter (7½ ft.) as that Mr. Garforth had erected in 1906 at the Altoft's colliery, for experimental work. This gallery was but 78 ft. long. The committee proposed to use a much

longer gallery, the investigation being estimated to cost £10,000. The Treasury declined to furnish funds so the Coal Owners Association undertook to provide funds for the gallery. The location selected was Altofts and Mr. Garforth, a member of the committee, gave personal supervision. Dr. R. V. Wheeler was appointed chemist. The objectives were:

1. The demonstration of the explosive nature of a mixture of coal dust and air without the presence of inflammable gas.

2. The discovery of a preventive against, or remedy for, such explosions.

3. The investigation of the chemical and physical phenomena accompanying coal-dust explosions.

Various ingenious instruments for recording pressure, the taking of gas samples automatically, time recorders, and circuit breakers were especially designed and constructed for the test work. A ventilating fan, coal and shale crushers, grinders, and other machinery were installed. The apparatus was quite different in detail to that employed by Taffanel, although the objectives were the same. Subsequently the United States borrowed ideas from both developments in designing its own apparatus for use in the Experimental Mine.

The first tests in the Altofts gallery in the nature of demonstrations of coal-dust explosibility began on May 12, 1908. On June 13, an experiment was made with a stone-dust zone, on the return side of the 369-ft. coal-dust charge, and a "dustless" zone on the intake side. The flame traveled only 44 ft. into the stone-dust zone, but in the dustless zone, after traversing 110 ft., the explosion burst out two plates in the gallery wall. After similar results had been obtained when the stone dust was on the intake side, the owners of the Altofts colliery were convinced that stone dusting was a practical undertaking and proceeded to apply it in their mines.

Dr. Joseph A. Holmes and the author visited the Altofts gallery in the latter part of July, 1908, and saw similar tests to those just described. These and other tests appeared to justify Mr. Garforth's long contention that stone or rock dust was effective in preventing coal dust from igniting or propagating an explosion.

British Coal-Dust Committee's Conclusions Favoring Stone Dusting

The Altofts gallery testing continued through 1909, attracting the attention of the mining public throughout the world. An extensive report was published, in 1910, strongly advocating stone dusting. The committee concluded, regarding the value of stone dust, that it acts more as a diluent, thus preventing ignition, than as a specific deterrent in stopping an explosion that has once started. This conclusion does not seem entirely in accord with the tests just mentioned. The

Date	Place	Name	Diagram of Gallery	General Remarks
1803	Britain	Buddle	Wallsend Colliery Explosion, September, 1803	"The workings were very dry and dusty and the survivors who were the most distant from the point of explosion were burnt by the shower of red-hot sparks of the ignited dust which were driven along by the force of the explosion."
1845	Britain	Faraday	Lecture at Royal Institution	Showed by experiment at a lecture at the Royal Institution, London, on Jan. 17th. 1845, that by taking coal dust and adding it to a flame, there was a marked difference in the combination as compared with a flame without dust
1875	France	Vital		Glass Tube { Length = 6 ft. 7 in. Diameter = 1.38 in.
1875	Britain	Galloway		Gallery made of wood { Length = 18 ft. 9 in. Width = 6 in. Height = 1 ft
1876	Britain	Hall & Clark	Adit 135 ft. long,	going from the surface at the crop of a coal seam
1878	Britain	Marreco, Morrison & Cochrane		Gallery made of wood { Length = 24 ft. Width = 6 in Height = 1 ft.
1879	Britain	Chesterfield Institute		Gallery made of wood { Length = 82 ft. Width = 1 ft. 4 in Height = 1 ft 6 in
1880	Britain	Galloway		Gallery made of wood { Length = 126 ft. Width = 2 ft Height = 2 ft.
1884	Germany	Prussian Commission		Gallery made of wood and strenghened with iron bands Axes = 5 ft. 8 in. and 3 ft. 11 in. Length 167 ft 3 in
1890	Britain	Hall	Experiments in a shaft 8 ft. diameter and 630 ft. deep (Third Series)	
1893	Britain	Hall	Experiments in a shaft 7 ft. diameter and 150 ft. deep (Fourth Series)	

Galleries in which experiments are at present being conducted.

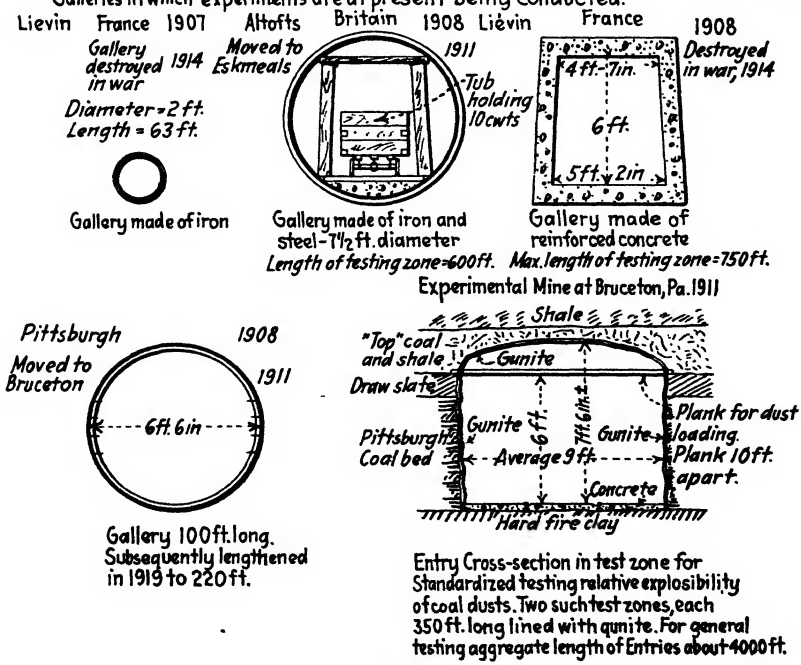

FIG. 1.

committee further states "It would therefore seem advisable not to employ zones of any description, whether watered, dustless, or stone dust, in spite of the good results that have been given by the last-named in dealing with an explosion that has traveled 275 ft." This point of view brings the conclusions of the committee in some degree of opposition to the conclusion of Taffanel, published in 1910, but the conclusions regarding ineffectiveness of zonal treatment is supported by the testing in this country at the Experimental Mine.

Large Gallery Testing in France

The General Council of Mines of France, an official body, published on August 1, 1907, a statement (in which by implication the explosibility of coal dust is admitted in contradiction to the official attitude prior to the Courrières disaster) that owing to the difficulties in general watering, as practiced in Germany, and its doubtful results, it was advisable that the firedamp commission examine the merits of schistification of coal dust, or mixture with other inert substance, that would perhaps be a practical means of preventing inflammation.

When testing in the large-size gallery at Liévin was started in 1908, some ignitions were apparently prevented by as little as 10 per cent. of shale dust. We now know that, unless these tests were being made with a low-volatile coal or semianthracite, there must have been some other reason for non-ignition. Apparently larger proportions of shale dust were not considered practical because the conclusions of Taffanel (published April, 1910) were that in considering watering or rock dust treatment in "dispersed form" it is more difficult to stop an explosion than to prevent it from starting.

Taffanel Proposes Water or Stone Barriers

He stated that "if the schistification or watering is in concentrated form, the method is successful in the immediate extinguishment of the explosion." By this Taffanel referred to what was termed a dust curtain or arresting barrier (arret-barrage) which in its first form was a heap of dirt. Then he tried troughs of water and also developed his shale-dust barrier consisting of ten, later fifteen, shelves across the roadway and near the roof, loaded with shale or cinder dust; the total loading on the shelves to be 4 hectoliter of inert dust per square meter (1.31 cu. ft. per sq. ft.) of cross-section of the passageway.

Explosion Disasters in United States

In 1906, there were no explosion disasters of magnitude, but there were 10 costing over 10 lives each, the largest at Pocahontas, with 36 deaths. However, the large number of shot-firers' explosions continued.

The year 1907 opened with four disasters in 11 days, killing at Primero, Colo., 24; at Penco, W. Va., 12; at Fayetteville, W. Va., 85; and at Thomas, W. Va., 25. Then no large explosions, other than shotfirers' explosions and one larger disaster at Whipple, W. Va., with 18 deaths, occurred until December, when there were five major disasters, killing at Naomi, Pa., 34; at Monongah, W. Va., our greatest explosion disaster, 358; Yolande, Ala., 16; Darr, Pa., 239; and Carthage, N. M., 11—a total of 658 for that month.

These disasters coming after the Courrières disaster and other explosions in Europe, caused a general belief that there must be some mysterious reason for these occurrences, one after another. Congress therefore, appropriated funds for the investigation of mine accidents and particularly mine explosions. This was the first time a Federal appropriation relating to the technical mining investigations had been made. The work was placed in the Technologic Branch of the U. S. Geological Survey, with Dr. Joseph A. Holmes as chief of the branch. The appropriation was available on July 1, 1908. Doctor Holmes meantime planned the organization of the investigation and had an explosives engineer, Clarence Hall, visit explosives testing stations in Europe, to gather data on testing apparatus. As the author had experience in explosion investigations, Doctor Holmes invited him to join the work and they both immediately went abroad to examine the new coal-dust testing galleries and methods then being followed for accident prevention underground.

In 1908, watering was not generally used in mines, except in German mines where sprinkling was mandatory. Yet German mines continued to have widespread explosions as at the Reden colliery, in the Saar, in 1907, with 150 fatalities, and at the Radbod colliery, Westphalia, in 1908, with 348 fatalities.

It was beginning to be accepted that extensive mine explosions would not occur unless coal dust other than anthracite was present, because these explosions traversed the intake entries, which usually were the haulage roads, rather than traversing the return entries which might have some firedamp but usually were not used for haulage, so did not have coal dust. At that time, so-called "flameless" or "safety" explosives were being required in European mines that were rated as gaseous or dusty, and this included practically all of the Continental mines and most of the British. Safety lamps were always required in deep Continental coal mines and in most mines in Great Britain.

Meantime, a gallery was erected at Pittsburgh, Pa., in connection with a newly established mine experiment station on the "Arsenal grounds." The gallery was 6½ ft. in diameter and 100 ft. long, and was used for testing explosives in the presence of firedamp or coal dust or both together. It was also used for preliminary tests of coal-dust explosibility.

Explosibility of Coal Dust

Starting in the fall of 1908, the author conducted tests of a preliminary character on the relative explosibility of particles of different sizes of Pittsburgh coal. He tentatively concluded and reported that what passed through a 20-mesh sieve should be considered as "dust." This definition of size later proved satisfactory in the experimental mine testing and has since been used as the Bureau of Mines standard coarser limit for all coal and rock particles specified or tested as dust. The British Mines Department later specified safety-lamp gage −28 mesh as its larger limit. The least unit amount of Pittsburgh dust of the "pulverized" size (through 200-mesh) that would ignite from a blown-out shot of black powder was also determined, tentatively. The amount of water required to make coal dust too wet to propagate an explosion was tested and found to be much higher than had been thought necessary. It required about 30 per cent. of water in the mixture of pulverized dust to prevent the raising of dust into a dust cloud that would propagate an explosion. This was later confirmed by the British testing at Eskmeals. However, smaller percentages of water are necessary to allay coarse dust but in any case the amount of water present must reduce the dust to a mud. Some testing of a preliminary nature of the relative explosibility of dusts of different chemical composition was done; also tests of the effect of inert material were made.[7] The results were published in Bulletin 425.

Permissible Explosives Testing and List of Approvals

Meantime testing of so-called safety explosives was begun and by the end of 1908, a schedule of tests for "permissibility" of explosives for use in gaseous and dusty mines were issued. Soon afterward, testing was begun of explosives submitted by manufacturers, who assisted this development in every way. By May 15, of twenty-nine submitted seventeen were approved. The Bureau having no mandatory, but only recommendatory, powers, the substitution of "permissible explosives" for black powder and dynamite was slow at first but later increased rapidly, through the initiative of the coal-mine operators and the favorable attitude of State inspection departments, until now there are practically no mines rated as "gaseous" that do not use "permissible explosives."

Explosion Disasters in United States, 1908–10

No general change in coal-dust neutralizing methods had taken place and many small explosions as well as large disasters occurred, in 1908, in the United States. The largest were at Hanna, Wyo., with 59 deaths;

[7] The Explosibility of Coal Dust. George S. Rice *et al.*: U. S. Geol. Sur. *Bull.* 425 (1910). Revised and reprinted as Bur. of Mines *Bull.* 20 (1911).

Mariana, Pa., with 154 deaths; and Lick Branch, Dec. 29, with 54 fatalities. These were followed in 1909 by the Ziegler mine disaster, with 26 deaths, and a second explosion at Lick Branch, only 14 days after the first, with 69 lives lost. The year 1910, also, had numerous small explosions and some large ones; Primero, Colo., with 75 deaths; Mulga, Ala., with 40; Palos, Ala., 83; Starkville, Colo., 56; and Delagua, Colo., 79. Many of these mines employed watering or sprays extensively, notably at Mulga, and the levels and stope of the pitching Palos mine were naturally wet, though the rooms and chutes were dry.

1911–1920

The early part of this decade was marked by intensive large-scals gallery testing in France, England, Germany, and in a mine in thie country. Great Britain and the United States experienced disastrous explosions, but France and Germany had few disasters.

The United States continued using the watering system, ineffectively in most mines. But the use of permissible explosives in gaseous mines and the introduction of approved or permissible electric undercutting machines in some mines prevented conditions from becoming worse with rapidly increasing mine production. In Great Britain, a few mines started to stone dust but most mines relied on eliminating sources of ignition, as the Altofts tests had not yet carried general conviction. French mines, with approval of the Government, put Taffanel's recommendations for "shale barriers" into effect with good results except in the gaseous La Clarence mine, where they failed.[8] In Germany, they continued extensive watering and hydraulic sand filling began to be extensively used, which helped watering. The great reliance of the German engineers, however, was in preventing sources of ignition.

British Coal-dust Investigations

The Altofts gallery tests were suspended in 1909 and the report of the Coal Owners Committee was published in 1910. The Government decided to take over the work and, in 1911, the gallery was removed to Eskmeals, Cumberland, where intensive testing of dust mixtures under the direction of Dr. R. V. Wheeler was carried on from 1912 to 1915, and a series of most valuable reports was issued, the concluding report recommending generalized stone dusting. Barriers did not meet favor.

French Coal-dust Investigations

The Lievin gallery, under Taffanel, was in active use until work was stopped, in 1914, by the great war. The gallery soon after was

[8] M. Taffanel ascribed this failure to insufficient inert dust in any one set of barriers and it did not destroy his confidence, or that of the mine operators, in the general principle of barriers.

destroyed by bombardment. Taffanel's investigations were largely directed to determining the effect of different mixtures of inert dust with coal dust and for different kinds of coal dust. He also carried on some confirmatory tests in an old gallery of the Commentry mine. He evolved formulas, from his data, to be applied to different categories of coal dust and for different conditions; which were to be used by the different mines according to the kind of coal mined, as regards volatile combustible and other conditions. These were gradually taken up by the more progressive mines. As his work progressed, shale-dust barriers were standardized but he then took the position, which the author had taken, that they were secondary defenses, or to be used where difficult to use generalized rock dusting.

German Coal-dust Investigations

In Germany, a gallery erected, in 1911, by the Westphalian Syndicate under a Government engineer, Beyling, carried on testing of water curtains, of wet peat along the sides, but did not take up, the author understands, rock-dusting methods until after the war.

United States Coal-dust Investigations

In the United States, after the preliminary testing in the 100-ft. gallery (in 1908–9), it was decided that little more could be done until either a longer gallery or, what was really desired, a mine could be obtained. Meantime, the author and his associates investigated with the greatest care all mine explosions, and there was ample opportunity from the number which occurred. Bulletin 425[9] had described both wet and dry methods of treating coal dust for explosion prevention. Miners' Circular of the Bureau, issued in 1911, although emphasizing rock dusting, also gave both methods, as, until more testing had been done, the Bureau was not prepared to discriminate officially.

In 1910, the Bureau of Mines was organized by a Congressional act, and took over the functions of the Technologic Branch of the U. S. Geological Survey, and Doctor Holmes was appointed Director.

Doctor Holmes was heartily in favor of conducting tests in a mine, not only because the results of tests would be more convincing to mining men, some of whom were skeptical of the gallery tests abroad and at Pittsburgh, but because the arrangements of rooms, entries, crosscuts, etc. in commercial coal mines, together with their conditions of temperature, rough walls, etc. could not be duplicated in surface galleries. The adoption of a mine for testing purposes has been fully justified and, in fundamentals, the test results have been accepted by European investigators.[10]

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[9] *Loc. cit.* (1911).

[10] Reasons for establishing the Experimental Mine were given in a paper read before the Western Society of Engineers (Chicago) 1910.

Experimental Mine Development

After a futile search for a suitable abandoned mine within 10 or 12 miles of the Pittsburgh Station, the present Experimental Mine near Bruceton (10 miles from Pittsburgh, Pa.), in the Pittsburgh coal bed was started from the outcrop in December, 1910. The mine and subsequent testing up to October, 1914, were described in a paper before this Institute of that date and in Bureau publications.[11]

In September, 1912, with the object of interchange of information and advice as to the best methods of testing in the Experimental Mine, an informal conference of mine-experiment stations was called at

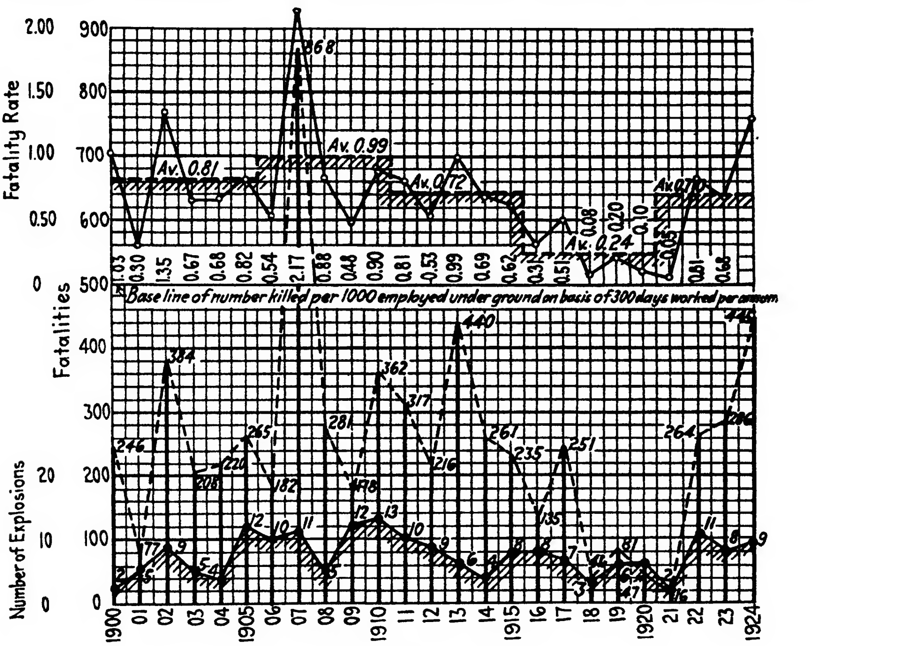

Fig. 2.

Pittsburgh; it was attended by representatives of Austria-Hungary, Belgium, France, and Germany, and unofficially by England. Demonstration tests were made at the Experimental Mine and the various problems relating to methods of testing coal dust, mine gases, explosives, safety lamps, etc. were discussed.[12] Those who are interested in studying the different points of view on methods of testing in Great Britain and the United States in the coal-dust question should read the discussion of a paper that the author gave, by invitation, to the (British)

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[11] Bureau of Mines *Bulls.* 44 (1912); 56 (1913); 82 (1914); 167 (1922); and *Tech. Paper* 84 (1915).

[12] International Conference of Mine Experiment Stations (1912). Bur. of Mines *Bull.* 82 (1914).

Institution of Mining Engineers in 1915, entitled "American Coal-dust Investigations."

The Bureau's experiments were directed:

1. To determining the fundamental factors of ignition and propagation of coal-dust explosions and the mechanics and chemistry relating thereto: (*a*) with no firedamp present; (*b*) in the presence of firedamp. The conduct of the work underground permitted the testing of coal dust with different percentages of firedamp (natural gas, 85 per cent. methane) which had not been systematically done in European galleries, and found that firedamp had an important influence proportionate to the amount of inflammable gas present, on both ignition and propagation.

2. To determine methods of preventing and limiting explosions in which were tried: (*a*) Methods of laying the dust to prevent its rising in the air, by wetting, humidifying, and deliquescent salt sprinkling; (*b*) neutralizing the explosibility of the coal dust, by strewing enough inert or non-combustible dust, which would rise into the air with the coal dust—in other words, stone dusting, or as the Bureau early termed it (1909) rock dusting; (*c*) limiting an explosion by dustless zones, watered zones, rock-dust zones, and rock-dust barriers, both simple shelves such as Taffanel used, and the enclosed barriers, which the author designed—both depending on the "pioneering" air wave to function.

The findings in these investigations are reported in detail in a Bureau of Mines bulletin.[13]

Status of Testing at Experimental Mine During and Following War, to 1920

The most important inclusions are stated in the summary of the paper. The bulk of the explosion testing was done from 1913 to 1916, inclusive. When the United States entered the war, early in 1917, as in the countries previously engaged, all energies of Government research bureaus were directed toward war problems and the Experimental Mine and its personnel were engaged in various special problems, such as sound ranging, development of liquid-oxygen explosives for industrial uses, if nitrates imports became more difficult because of submarine warfare, and like inquiries. Following the close of the war, coal-dust investigations were further interrupted by use of the Experimental Mine for ventilation testing to determine fundamental factors with reference to mine ventilation and for investigations concerning the unique ventilation problem presented by the New York-New Jersey Vehicular Tunnel project, now under construction. A tunnel on about one-third scale in cross-section

[13] George S. Rice, L. M. Jones, W. L. Egy, and H. P. Greenwald: Coal-dust Explosion Tests in Experimental Mine, 1913 to 1918. Bur. of Mines *Bull.* 167 (1922).

EXTENSION	
MARK	DATE
A	12-10-13
B	2-16-14
C	7-23-14
D	1-30-15
E	10-1-15
F	6-20-16
G	6-25-17
H	6-10-18
I	6-16-19
J	7-15-20
K	11-1-21
L	9-1-22
M	5-15-24

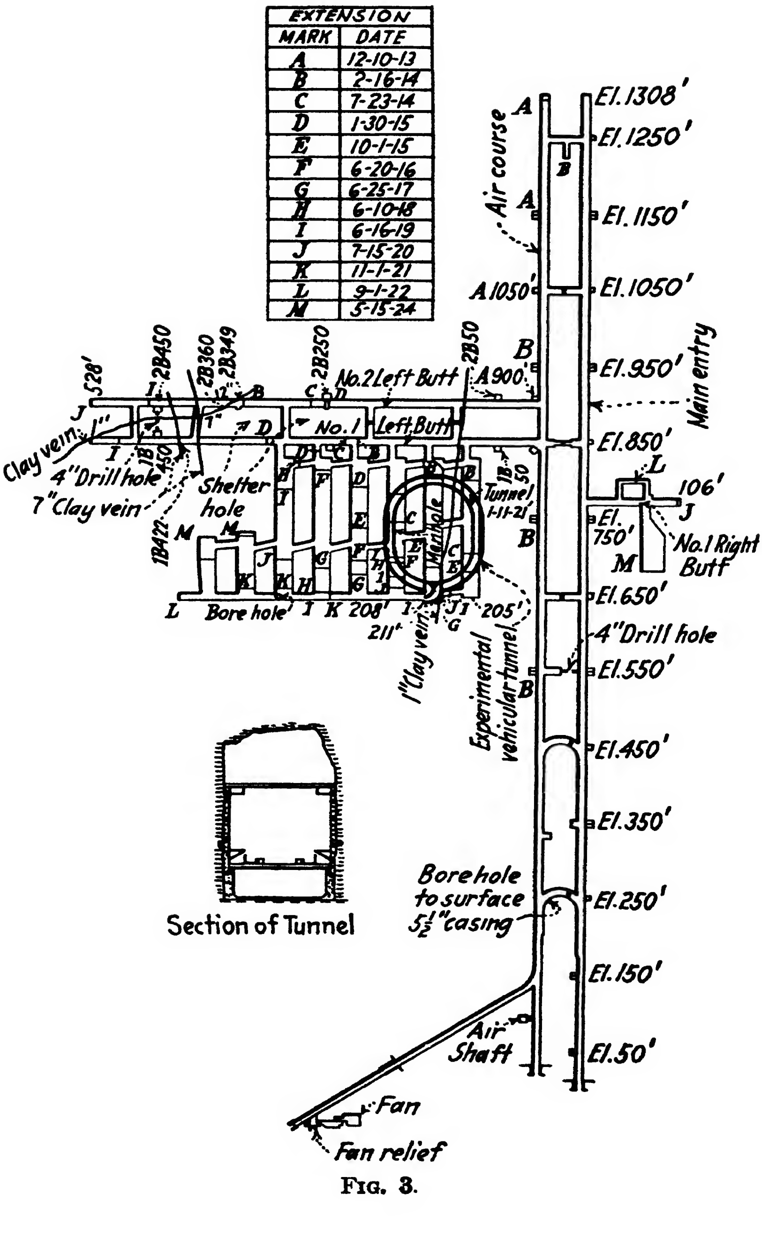

FIG. 3.

was constructed in the mine and a proposed new method of ventilation, transverse instead of longitudinal, was tested, using ten automobiles, with elaborate ventilation, temperature, and chemical control.

European Coal-dust Investigations Following the War, up to 1920

Comparatively little large-scale explosion testing was done in Europe for several years after the war. The French Liévin gallery has not been replaced; in fact, the French authorities are quite satisfied with the reports and conclusions of M. Taffanel, although while on his visit to the Experimental Mine in 1914, just prior to the war, where he studied and advised on our methods, he stated that there were so many factors in the coal-dust explosion phenomenon that it would take an indefinite number of years of experimenting to reach satisfactory answers to some of the countless problems.

The British carried on some further testing at Eskmeals, but their attention was primarily directed to laboratory investigations of fundamental physical and chemical factors.

British Stone-dusting Order of 1920

As a result of the report (published Sept. 13, 1914) by the Explosion in Mines Committee just prior to the war, and perhaps also, it is surmised, because mine-explosion disasters were occasionally occurring, as for example at the Minnie pit, Staffordshire, in 1918 with 155 deaths, the Mines Department issued General Regulations effective Jan. 1, 1921, requiring that:

> All mines in which coal other than anthracite is worked, except mines of which the floor, roof and sides of the roads are naturally wet throughout . . . shall be treated with incombustible dust in such manner and at such intervals, as will insure that the dust on the floor, roof and sides throughout shall always consist of a mixture containing not more than 50 per cent. of combustible matter . . . or, if treated with water, that the dust . . . is always combined with 30 per cent. by weight of water in intimate mixture . . . provided that the percentage of incombustible dust required . . . may be reduced by an amount equivalent to the percentage of water present in the mixture.

The application of such an amount of water, as called for, was generally thought impracticable of attainment, apart from the question of damage to roof and ribs, which in most deep mines are very dry. Accordingly the order was regarded equivalent to requiring generalized stone dusting and the greater number of mines proceeded to introduce it.

The other salient points of the order are that the stone dust used shall be of a fineness that 50 per cent. will pass through a 200-mesh sieve; that the stone dusting shall extend within 10 yd. of the coal face and that "representative tests," which assume systematic sampling,

"shall be made by the management at intervals of not less than once a month, and the results shall be posted at the pit head."

Amended British Stone-dusting Order of 1924

A recent order (Nov. 20, 1924) amended the previous order by making no exception in respect to mines in which the roads are naturally wet, and making them subject to the requirement of 30 per cent. of water in the mixture. This change was probably brought about by occurrence, since the order of 1920, of a number of explosion disasters in "naturally wet" mines.

Another important amendment was that the floor, roof (including roof timbers), and sides respectively should receive separate consideration and representative samples taken separately; that is, each on analysis must show no more than 50 per cent. combustible content, or else the mixture should contain 30 per cent. or more of water.

The representative samples are to be taken "over an area of road not less than 50 yd. in length" and each sample (of floor, roof, and sides, respectively) must be well mixed, and a portion of the mixture sieved through a 28-mesh sieve. The resulting sample, as under the old order, is weighed, dried to determine moisture, and incinerated to determine loss of combustible matter, or if the method is not appropriate for the kind of dust (limestone for example) some other method may be prescribed. The tests must be made monthly or more frequently and the results must be not only posted at the pit head, but recorded in a book kept for the purpose.

It is evident that the new order is considerably more drastic than the old, in requiring that the dust on floor, roof, and sides, respectively, each have less than 50 per cent. of combustible content. It will tend to make the average non-combustible content in a given section or zone of roadway well over 65 or 70 per cent., as in bringing the dust on any one of the three, floor, roof, and sides up to requirements, it is likely to cause excess in the other two. The alternative method, watering, is I think practically impossible, if the requirements are met.

Progress of Rock Dusting in the United States

Some of the disasters investigated by the author between 1908 and 1914 brought increasing conviction that watering or natural dampness would not give protection from coal-dust explosions propagation. These disasters were:

	Fatalities	
Nov. 29, 1908, Marianna, Pa	154	
Jan. 13, 1910, Primero, Colo	75	
April 20, 1910, Mulga, Ala	40	
May 5, 1910, Palos, Ala	83	(slope wet)
April 8, 1911, Banner, Ala	128	
Oct. 22, 1913, Dawson, N. Mex	263	
Nov. 18, 1913, Acton, Ala	24	
April 28, 1914, Eccles, W. Va	181	

Other mines, in which explosion disasters occurred, which were personally investigated by the writer during this period, prior to explosions had done little or nothing regarding watering, but the mines in the foregoing list were said to have employed systematic sprinkling or else, in a couple of cases, the mines were considered to be naturally wet, and were wet in places even after the explosion.

The publications prepared by the writer and associates from 1911 on, increasingly emphasized rock dust as one method of coal-dust explosion prevention and pointed out that if watering was done the dust must be so wet that it was mud, or it would not be effective.

Many Bureau reports on individual mine disasters recommended rock dusting. These reports are made only confidentially to the mine operator concerned, because it is the function of the respective State department to investigate officially and legally require such improvements or changes as decided upon.

The late William J. Murray, of the Victor Fuel Co., of Colorado, with his assistants, decided to try dusting with adobe in one of its mines, following a conference between Mr. Murray and the author at Trinidad, Colo., while the latter was investigating the Primero mine explosion of Jan. 31, 1910.

In 1911, Mr. Murray started adobe dusting in the Delagua Mine, Colo., in the main trolley haulage roadway, applying it with a fan distributor mounted on a mine truck that was moved by a trolley locomotive. The dusting was continued for some years until Murray's retirement and death, when it was dropped. A few other companies in the West and the East also made preliminary trials but did not follow it up.

In 1916, after a year's trial, with favorable results, of a stretch of rock dusting in a commercial mine in the Pittsburgh district, the Bureau engineers thought that the time had come for further developments and issued a circular letter to manufacturers of crushing machinery (which was also published in *Coal Age*, April 15, 1916) stating, "As a result of mine-explosion experiments at the Experimental Mine and explosion-prevention investigations in the field, the Bureau strongly recommends the use of finely crushed or pulverized rock dust having no combustible

matter, or a very small percentage, as a preventive for coal-mine explosions." The circular suggested that this was a new field for crushing or pulverizing machinery; also that there was need of a mechanical rock-dust distributor. The distributor at the Experimental Mine was described and illustrated and the suggestion was made that the flexible discharge pipe could be connected with pipes through crosscut stoppings for rock dusting back entries that had no tracks.

This proposal had no apparent results. In view of the present enthusiasm of many for rock dusting, it is difficult to explain why mine operators did not take it up earlier. Perhaps it may be explained on the ground that the Bureau of Mines in its formal publications had not declared, until later, a strong preference but had described wetting methods as well as rock dusting for explosion prevention. Another reason may be that prior to and during the world war, the operators were too busy to think of new methods and for four years following the war to 1922 the United States experienced no major coal dust explosions.

Experience of Old Ben Coal Corporation with Rock Dusting

In 1918, the Old Ben Coal Corporation of southern Illinois, of which J. E. Jones is the safety engineer, had a bad explosion that killed all men in the mine (fortunately there were but 17 men in the mine at the time). The company sent samples of its coal to the Experimental Mine for testing. Rock dust and rock-dust barriers were successfully demonstrated. The company decided to use barriers and Mr. Jones designed and installed some on the same principle but slightly differing from two of those described in the author's paper of 1914. The company has since had seven explosions, all of which were stopped by barriers, saving hundreds of lives.

However, as some men were killed in these explosions inby or between barriers, the company decided, about a year ago, to use generalized rock- or shale-dusting. The shale was obtained from the roof and Mr. Jones has developed a rock-dusting machine, the fan motor being driven from the trolley wire.

Official Approval by the Bureau of Mines of Rock-dusting Method

In 1922 and 1923, there were sixteen explosion disasters, in which coal dust was considered to be the cause of propagation, causing 530 fatalities. This aroused anxiety, especially as at several of these mines efforts were made by the respective operators to sprinkle thoroughly.

Director Bain decided, in the spring of 1923, that the time had come for the Bureau of Mines to take a decided stand, that watering even with the best of intentions had not proved efficient as practiced. Whereas,

on the basis of the Bureau's tests and recommendations of its investigators in the coal-dust question, generalized rock dusting had been demonstrated to be a positive means of preventing explosions.

Investigations of Rock-dusting Methods in Great Britain and France

The writer was detailed to visit European mines on certain matters and, in particular, to study the methods of rock dusting being practiced in Great Britain and France. Typical mines in different districts were visited and he was greatly impressed with what was being done at most of the mines, in the thorough way rock dusting had been done. In one respect the problem in Great Britain is easier, as the longwall method is almost universal and hence there is considerable natural stone dusting on the newer roads or roads near the faces and in the air courses. Also they do not have rapid haulage nor the hazards of trolley wires and bare power cables. Nor is there the spalling off of the coal ribs and coal roof, as in many American mines.

One of the features of stone-dusting practice in Great Britain that most impressed the author was the method of systematic sampling and recording and of sending monthly duplicate reports to the Inspector of Mines, so the condition of the roadways in respect to the coal-dust hazard was under constant supervision by the mine owner and checked by the Government inspectors.[14]

Coöperation with Great Britain on Mine-safety Research (1924)

Following informal conferences in the summer of 1923 at the Eskmeals Station, with Dr. R. V. Wheeler, in charge of research work, under the Safety in Mines Research Board, and later with that committee, a proposal was made by the Secretary for Mines to the Director of the Bureau of Mines through the Secretaries of State and Interior for a coöperation on research relating to safety in mining.

This proposal was accepted and an interchange of information and of personnel was arranged. Under this coöperation H. P. Greenwald, physicist in charge of the technical matters in the Experimental Mine investigations, was detailed to Great Britain this last summer and fall, and was placed, by Doctor Wheeler, in charge of the explosion-gallery testing for that period. Interchange of laboratory research matters has been going on with great advantage to both sides of the coöperation.

Doctor Wheeler and Henry Walker (then deputy, now chief inspector of mines) visited this country a year and a half ago to make further

[14] The author's report on rock dusting to prevent coal-dust explosions in Great Britain and France was issued in February, 1924, as Bur. of Mines *Bull.* 225.

plans for the coöperation and they assisted in conferences with mine operators and mining engineers on rock dusting held at Pittsburgh, Chicago, and Benton, Ill. These conferences were most influential in bringing to the attention of the mining men the merits of rock dusting, as practiced in Great Britain, in the prevention of major explosions in rock-dusted mines, in contrast with disasters that had occurred in so-called naturally wet mines. Subsequently, conferences on rock dusting were held in the Rocky Mountain coal-mining centers, which were attended by J. E. Jones, who kindly served the Bureau as consulting engineer in carrying on the rock-dusting campaign. Since these conferences, all the coal-mining institutes that have had meetings have devoted at least one session to rock dusting.

One of the most helpful features in the advancement of rock dusting has been the giving of credits by the accident liability insurance companies to mines using rock dusting, thus lessening the premium paid by mining companies. The state of Utah has also set an example by requiring rock dusting and the Mine Inspectors Institute of America, in a meeting held last May (14 and 16) at Cincinnati, made recommendations prescribing it in a tentative model for State mine regulations.

Tentative Specifications of Bureau of Mines for Rock Dusting

Last spring, the Bureau issued tentative specifications on rock dusting (Serial 2606, by Rice, Paul, and Sayers). Meantime, the Pittsburgh laboratory of the Bureau has made hundreds of microscopic and chemical analyses to determine the suitability of the rock dust on the basis of the tentative specifications and the Chief Surgeon, Dr. R. R. Sayers, has been conducting physiological tests to determine advisable limits of free silica and the effect of different dust mixtures. Recently, a committee of the Institute, Howard N. Eavenson, chairman, in coöperation with the Mining Standardization Correlating Committee, has undertaken to draw up standard specifications.

Future Coal-dust Explosion and Prevention Investigation

While the most important factors of coal-dust explosibility are now fairly well known, the infinite number of problems, through different combinations of coal dust, firedamp, inert dusts, and methods of ignition, have hardly been touched. For example, coal-dust characteristics vary much more than the varieties of coal beds from which the dust is formed, both in physical structure of the particles and in chemical composition, because it may be formed from softer layers or benches different from the average composition of the whole bed.

Then there are differences in ash material, whether ash of composition or external, and the effect of water of composition in contrast to adsorbed and external wetness that must be studied. Investigators have only

slightly touched on questions of side openings from a roadway and the increase in cross-section near the initiatory point of an explosion, also the effect of bends and irregularities as compared with straight entries. The effect of timber in producing eddying on propagation of an explosion and of large falls of roof, which in certain cases as at the Benwood, W. Va., explosion of April, 1924, appear to stop the explosion in that direction. This refers to extensive falls of roof due to timbers being knocked out by the pioneering wave. Again, there is the effect of reflected waves in stopping an incipient explosion. Finally, there are the problems of the relative position of coal dust and rock dust, and of the position of rock-dust barriers, with reference to side openings and enlarged places in the immediate vicinity. The importance of size of rock-dust particles has been studied but more information is needed. There is also the question how near the face must rock dust be carried under different conditions. For example, the British orders call for its distribution to within 10 yd. of the face, which in most instances means the longwall face.

Sampling to Determine Condition of Mine Dust

The method of sampling road dust in order to determine, from time to time, the amount of combustible in the dust is important. It is not a simple problem. The British orders contemplate only qualitative determination of the composition of the dust. The method was less important under the old order; but under the amended order, in which the dust on floor, roof, and sides are considered separately, the problem becomes more difficult. For example, a high combustible content of a few ounces of roof dust per linear foot of passage would offset the advantage of a very low combustible content of several pounds of dust per linear foot from the sides or floor, and would require redusting of the zone. This plan is in the interest of safety, but adds to the work and cost of rock dusting. The Bureau of Mines has hitherto recommended quantitative sampling, to include all the loose dust in a given section—roof, timber, sides and floor—to determine from the analyses or volumetric method,[15] the need of redusting in the particular zone.

Further, the British method of sampling the dust, which was observed in certain mines, is to take a number of grab samples along a given area 50 yd. in length and mix these together. The method recommended by the Bureau has been to take the sample cross-sectioning the passage, where there appears to be an average thickness of dust, to include all loose dust from roof, timbers, sides, and floor. It is gathered by scoop[16] and

[15] A. C. Fieldner, W. A. Selvig and F. D. Osgood: The Quick Determination of Incombustible Matter in Coal and Rock Dust Mixtures in Mines. Bur. of Mines *Tech. Paper* 144 (1918).

[16] A scoop designed by the author has a rubber edge and a 10-mesh sieve over the rear half with space below to receive the dust; the oversize is thrown away.

brush making a channel about 6 in. wide. The gross sample is screened, that passing through a 100-mesh sieve is sent to the laboratory; it is rescreened through a 20-mesh sieve, that passing through is considered dust and is weighed. Its weight is considered to be the average and its analysis the average composition, per unit of length half way to the next cross-section. The distance apart of such cross-section samples has not been specified. That question has been left to the judgment of the sampler, but it is understood that the nearer such samples are taken, the more nearly will their average represent a given area, or zone.

Manifestly neither of the foregoing methods is precise and it becomes a question which is the better, or whether some other method may not show the degree of hazard represented in a given zone. One suggestion has been the use of a vacuum cleaner and some trials have been made with

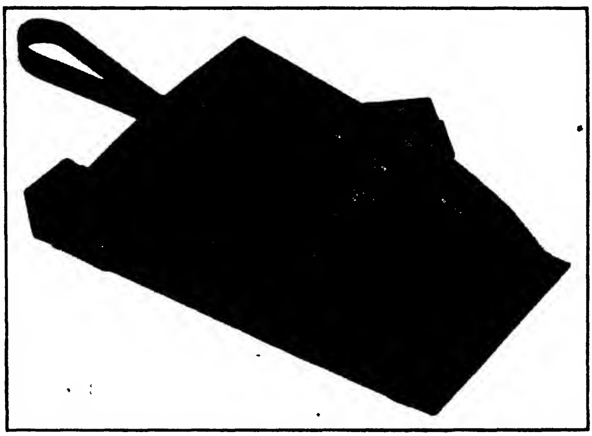

FIG. 4.

this, with favorable results, at the Experimental Mine in a zone of known composition, in contrast with cross-sectioning by channel as above described. The Old Ben Coal Corpn., it is understood, uses this method. It will require more experience in other mines under varying conditions of coarse coal and rock, which get mixed in with the dust material, before the best method of sampling to suit American coal-mining conditions is evolved. As yet, the importance of this problem has not been fully realized. Most of the mines concerned have taken up rock dusting so recently the question of need of redusting has hardly arisen where a thorough first dusting was done.

AMOUNT OF ROCK DUSTING REQUIRED PER UNIT OF ENTRY

This question depends on: (*a*) The amount of coal dust and natural inert matter present in an entry before rock dusting; (*b*) the explosibility hazard presented by the particular coal dust, which differs in volatile

combustible and ash content and moisture present; (*c*) size of particles as represented by the proportion of 200-mesh dust of the total dust (through 20-mesh); (*d*) whether the air current is intake, or if a "return," the percentage of firedamp normally present.

The Bureau's experiments have shown that it requires from 3 to 5 per cent. more non-combustible in the dust to offset each 1 per cent. of firedamp in a return. In this respect, the Bureau's results are very different from those obtained in the Eskmeals gallery. The British Committee reported that a small percentage of firedamp had no effect on explosibility.

Taffanel, from his Liévin tests, recognized that firedamp made a difference in explosibility of coal-dust mixtures and used different values for constants in his formula when applied to gaseous mines.

In order to give some idea of the quantity needed to those who have not used the method, the first application in an entry of ordinary size that has been thoroughly cleaned in advance should be not less than 2 or 3 lb. of rock dust, and preferably 4 lb., per linear foot. This if properly applied, by hand or by one of the dusting machines on the market, should fill with rock dust the crevices and recesses along the ribs and cover the top surfaces of timbers and projections.

Kind of Rock-dust Material

The Bureau investigations have shown that any dry, inert dust or dust with little combustible matter (under 9 per cent.) that does not cake in a humid atmosphere, is efficient as a coal-dust explosion prevention material, when used in sufficient proportion to obtain in the mixture with the coal dust from 50 to 75 per cent. non-combustible. The percentage depends, as before stated, on the character of the coal dust and its fineness. Obviously, the nearer the white road dust is the better will be its illuminating effect in an entry. Hence the Bureau has particularly recommended pure limestone, dolomite, and gypsum apart from the general freedom of these materials from silica.

Effect of Rock Dust on Health

As many materials proposed for rock dusting, including shales, contain much free silica, it has been considered advisable by the physiologists of the Bureau to recommend tentatively that dust containing over 25 per cent. free silica be not used, where it is liable to get into the air and be breathed. This specification would manifestly have no application to dust used in barriers or in disused workings or rarely travelled entries.

Dr. J. S. Haldane, the celebrated British physiologist, states, as a result of testing with animals, that the presence of coal dust in a mixture even in small proportions is helpful in neutralizing the effects of free silica. Dr. R. R. Sayers, chief surgeon of the Bureau, advises he is not yet prepared to express an opinion in this matter. For the past year his assistants have been carrying on extensive experiments on animals, but

such an investigation requires a long time before conclusions can be reached.

The most favorable outlook was that given by the British use of rock dust or "stone dust" in some mines for over ten years. Up to the time of the author's visit, the latter part of 1923, so he was informed, no claims for compensation had been made by miners, under the compensation act for occupational diseases, although a great volume of claims have been made for other physical ailments, real and fancied.

From personal inspection in haulageways in British rock-dusted mines the author would say that a trip of cars does not stir up nearly as much dust as does a vehicle on a dry or sandy road, and he noticed no disagreeable effect of breathing dust, as one often does on a dusty country road. Similar evidence has been reported in this country by observers in those mines in which rock dusting has been done. Nevertheless, it is desirable to use rock-dusting material with low free silica content so as to have the health hazard of the dust beyond suspicion.

Size of Rock-dust Particles

The experiments of the Bureau have indicated that rock dust with as much as 50 per cent. through 200-mesh is as effective as if the dust is all fine particles. Not until the percentage was as low as 30 per cent. was a difference apparent. The proper size of dust and questions of distribution by mechanical means and the cost of fine grinding is being much discussed by mining men. Some have contended that an extremely fine dust must be used, but, so far as explosion prevention is concerned, the need of extreme fineness has not been demonstrated by explosion experiments or by explosion experience in dusted commercial mines. Hence, the tentative specification of the Bureau for 50 per cent. through 200-mesh, which agrees with the British experience, appears reasonably safe for the present.

Rock-dust Barriers

As repeatedly stated, the writer and his associates agree that rock-dust barriers should be regarded as secondary defenses and are especially useful at strategic points—entrances to panels, connections with adjacent mines, and at the entrance to unsealed old workings. The writer also recommends they be used at intervals of from 1000 to 2000 ft. along haulage roads in addition to generalized rock dusting. The writer has observed in visting mines in this country, where barriers have been installed, that in many instances the experience obtained in actual explosion tests at the Experimental Mine has been disregarded and most of the barriers he has seen installed would not stop a *strong explosion.* They do not have enough loading, or they dump *en masse;* also

they are not arranged so that a *slow explosion* with low-pressure pioneering wave would dump them. Although he thinks he was the first to propose the use of, and to design, inclosed barriers, he believes that open Taffanel shelves would be better than many "inclosed" barriers recently observed.

Any one set of box or trough barriers or the concentrated barrier[17] relied on in a mine with no generalized rock dusting should contain about 100 lb. of rock dust per square foot of cross-section of entry. A barrier should not be placed in a wide place and, preferably, where there is not an enlargement of passage just inby or outby, as it functions by mixing its loading of rock dust with the coal dust stirred up by the pioneering waves and this is best accomplished in a restricted or normal sized passageway. It should be mechanically operated, so that it can be made to extinguish a slow explosion, by an air wave having as low a pressure as 1 lb. per sq. in.; if the surface is hinged along the edge the pressure effect would be halved. In either case, the pressure would be momentary, so inertia of the moving parts must be carefully considered in designing.

In considering a design of a barrier, certain other factors must be taken into account, among them the velocities of coal-dust explosions. The barrier should be designed so it will not, in dumping, drop its load in a compact mass that will prevent its mixing with the air, and will not drop all its dust before the flame arrives.

Velocity of Coal-dust Explosion

The pioneering air waves, or shock waves, that stir up the coal dust ahead of the flame of a coal-dust explosion, travel at the rate of a sound wave in a passage with rough walls and bends at 1100 to 1200 ft. per sec. The flame starts slowly from the ignition point, sometimes less than 100 ft. per sec., but rapidly accelerates except in a dust with low order of explosibility. In a fast explosion, with fine coal dust, the flame of explosive combustion travels at velocities of 2000 to 4000 ft. or more per second. The rate is accelerated for a specific dust mixture by the presence of firedamp. We do not know what occurs when a fast explosion catches up with the first shock waves started by the initiatory explosion, as this has not occurred within the length of main entry in the Experimental Mine; viz., 1300 ft. We assume it will check the velocity momentarily until the shock waves have again advanced at 1100 ft. per sec. to stir up the dust ahead without which prior mixing of coal dust in the air, an explosion must die away.[18] It has frequently been observed in widespread explosion disasters that the velocity of the moving zone

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[17] See *Bull.* 167 or *Tech. Paper* 84 for description of barriers.

[18] The pressure manometer curves also show that there is a compression of air, which in some records has attained several atmospheres, immediately in front of the flame; but we do not know that the time, less than one-hundredth of a second is sufficient to permit raising and mixing the coal dust in advance of arrival of the flame.

of explosive combustion, as indicated by relative violence, varies from point to point.

Restricting the Formation of Coal Dust

The formation of coal dust in a coal mine, all will agree, is inevitable, but the amount can be greatly restricted and the amount of rock dust needed lessened. Much in this direction can be done by using only tight mine cars, and preferably tight-end cars, by avoiding excessive use of explosions in breaking coal, and with machine mines, by loading out the "bug" dust before shooting. The plan, tried in the Birmingham, Ala., district and extensively adopted in Utah and elsewhere, of using water sprays playing on the cutter bars of machines, is commendable. The wetting down of the broken coal and of the face of hose, before loading the coal, as employed in Utah is also excellent. The use of automatic sprinklers on loaded cars at the entrance to sidings is a splendid practice, as the finest coal dust is formed along the roadways, and it is through the entries that an incipient explosion may become a widespread disaster. This use of water at the face and at special points there is nothing to conflict with rock dusting extending near the face.

Acknowledgments

In concluding, the author wishes to express his appreciation of the splendid work of his associates, in the Experimental Mine investigations; the late L. M. Jones, mining engineer, who heroically lost his life on Oct. 20, 1916, in mine-rescue work at the Barricksville, W. Va., explosion disaster; W. L. Egy, physicist, who was formerly in charge of instrument work; his successor H. P. Greenwald, physicist, who has shown great skill in handling the instruments and developing new types and who, because of his technical information about explosion testing, was placed in charge of the British coal-dust gallery testing at Eskmeals this past summer; H. C. Howarth, superintendent of the mine, whose practical knowledge and skilful handling of the mine and preparation for tests has been invaluable; and last but not in importance, James W. Paul, chief coal-mining engineer, who has undoubtedly investigated more explosion disasters than any one in the country and whose skill in unraveling the mysteries of mine explosions is unsurpassed. His work formerly lay in a different section of the Bureau's activities—in mine-rescue work, breathing apparatus development and safety-lamp testing, but since 1918, the coal-dust explosibility testing has been in his charge.

The author regards rock dusting as having really arrived now that many coal-mine companies, manufacturers of mining machinery, and mining engineers in commercial work or consulting capacity are taking up the development. Among the latter are T. J. Fear, J. T. Ryan, E. S. Steidle, and H. N. Eavenson in the East; J. E. Jones, in the Middle West; and D. Harrington, and others in the Rocky Mountain region.

APPENDIX

Details of the Tests at the Experimental Mine

The explosion test prepared for members of this Institute on Oct. 9, 1914, was a demonstration of the explosibility of coal dust and the effi-

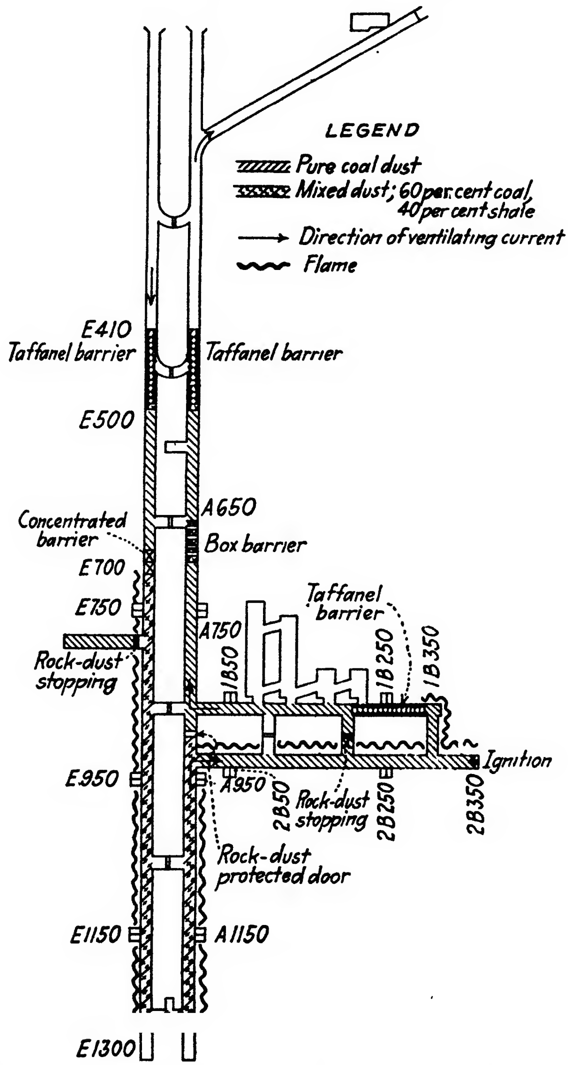

Fig. 5.—Arrangements for test witnessed by members of Institute at Pittsburgh Meeting, 1914. (Test No. 141.)

ciency of various rock-dust explosion-barrier devices. The visitors were members of the Institute also State mine inspectors from Pennsylvania, Ohio, and West Virginia, there being from 150 to 200 visitors present. A

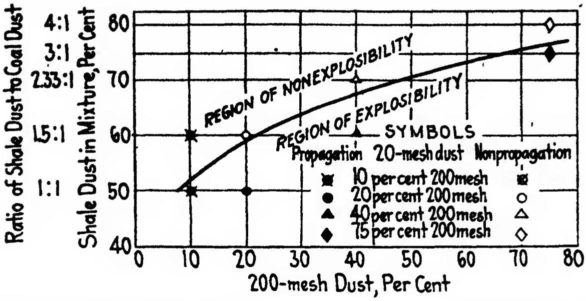

FIG. 6.—EFFECTS OF SIZE OF COAL DUST ON EXPLOSIBILITY OF PITTSBURG DUST.

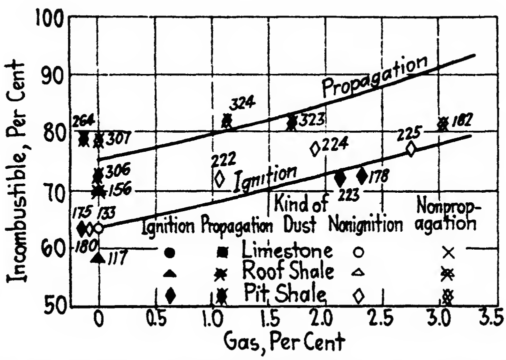

FIG. 7.—EFFECT OF SMALL PERCENTAGES OF GAS IN VENTILATING CURRENT ON EXPLOSIBILITY OF MIXTURES OF PULVERIZED PITTSBURGH COAL DUST AND VARIOUS INCOMBUSTIBLE DUSTS.

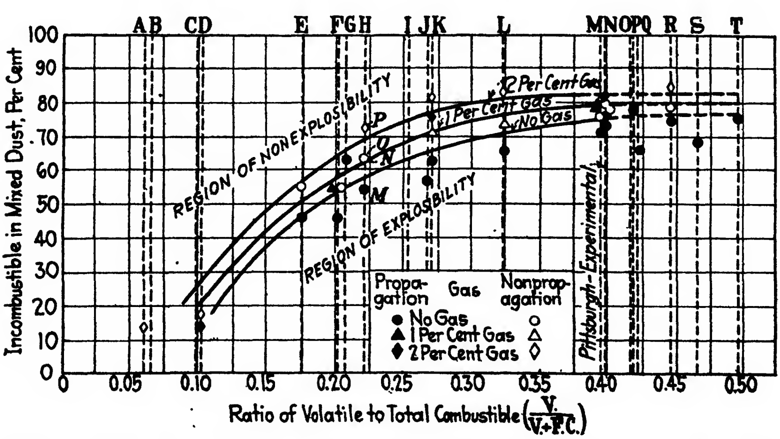

FIG. 8.—EXPLOSIBILITY CURVES FOR PROPAGATION TESTS WITH PULVERIZED DUSTS, SHOWING EFFECTS OF VOLATILE-MATTER CONTENT AND OF PERCENTAGE OF GAS IN AIR CURRENT; AS FIGURE IS SMALL, IT SHOWS ONLY A FEW OF THE TEST POINTS THAT CONTROL THE CURVES.

standard blown-out cannon shot was placed at the face of No. 2 butt (see Fig. 5). Pure pulverized Pittsburgh coal dust was loaded in No. 2 butt and in the 200 and 300 cut-throughs to No. 1 butt. A mixture of 60 per cent. pulverized Pittsburgh coal dust and 40 per cent. roof-shale dust was distributed in the air course from A875 to A1250, then through the 1250 cut-through and out the entry to E700. At a number of places barriers were installed to limit the flame. A Rice concentrated barrier was placed at the end of the zone at E700. Outby the concentrated barrier was a 200-ft. auxiliary zone of pure pulverized Pittsburgh coal dust, this being terminated by a 15-shelf Taffanel barrier. A rock-dust

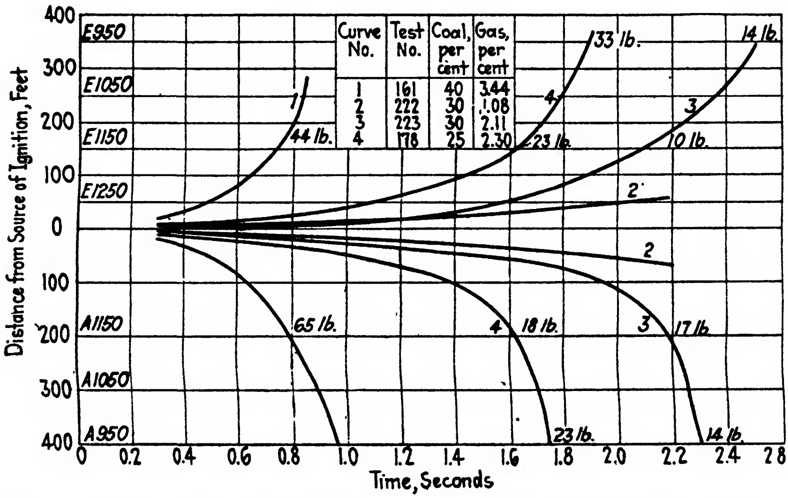

FIG. 9.—FLAME VELOCITY CURVES FOR IGNITION TESTS ON PULVERIZED PITTSBURGH COAL AND PULVERIZED SHALE WITH FIREDAMP PRESENT.

stopping was placed in the right butt turned from the entry at E775, the entire butt inby the stopping being loaded with pure pulverized Pittsburgh coal dust. A Rice rock-dust-protected ventilating door was placed at A875. Pure pulverized Pittsburgh coal dust was loaded from A875 to A700. A six-box barrier was placed at A700. Pulverized Pittsburgh coal dust was then loaded to A500, and a 15-shelf Taffanel barrier was placed at the end of this zone. A rock-dust stopping was placed in the 200 cut-through between No. 1 and No. 2 butts. A 15-shelf Taffanel barrier was placed in No. 1 butt from 1B 295 to 1B 205. No. 1 butt was loaded with pure pulverized Pittsburgh coal dust outby the Taffanel barrier.

The explosion was successfully originated at the face of No. 2 butt, traveled out No. 2 butt, thence inby in the air-course toward the face through the cut-through and out the entry to E700, all side branches therefrom being protected by various types of barriers. Every main barrier had a zone of pure pulverized Pittsburgh coal dust outby in order

to evidence any failure of the barrier. If flame would pass through the barrier this auxiliary zone would be ignited and a further extension of the explosion would result.

The explosion produced moderate pressures in the butt entry but built up considerable pressure in the main entry after traveling about 1200 ft., the pressure at station E750 being about 40 lb. per sq. in. All of the barriers operated and the flame was confined to the path originally intended for it. Most of the barriers were entirely destroyed by violence. The test was entirely successful as a demonstration of the operation of various explosion-stopping devices under varying conditions of velocities and pressures at the different points.

Economics of Rock-dusting Bituminous Coal Mines

BY EDWARD STEIDLE,* PITTSBURGH, PA.

(New York Meeting, February, 1925)

THOSE who have followed the rapid progress in rock-dusting bituminous-coal mines must admit that opinion crystallized during the year just closed in support of this preventive of coal-dust explosions. Up to 1924 only one mining company in America practiced rock-dusting on a large scale, but during 1924 forty-two companies had adopted this safety measure, and the "boom" is expected to extend over the next two or three years. Alabama is represented by 1 company, Colorado by 3, Illinois by 4, Kentucky by 1, New Mexico by 4, Pennsylvania by 20, Utah by 8, and Wyoming by 1. A total of about 500 miles of entry has been dusted. Illinois leads with 275 miles of dusted entries and Pennsylvania holds second place with about 175 miles. In each case there is a sense of great security, not only on the part of the operator but by the miner as well.

It is also interesting to note that during 1924 the compensation rating or inspection bureaus in twelve of our coal-producing states revised their rating schedules so that a credit would be given for rock-dusting. This credit ranges from 10 to 20 cents per $100 payroll.

Recent drastic federal and state regulations approved by mine operators made rock-dusting compulsory in bituminous coal mines in Utah, beginning July 1, 1924. Legislative action favorable to rock-dusting may be expected in other states. Colorado has already proposed a change in its laws, and Pennsylvania, Maryland, Washington, and West Virginia are giving the matter consideration. If the rock-dusting problem is handled properly and proves to be entirely successful, no mining man of any standing will delay applying it in his mine. State legislation regarding this matter may or may not solve the problem. At present, the mining companies that are rock-dusting of their own choice are doing it carefully and thoroughly. In Utah, some are doing it conscientiously, trying to get what benefits can be obtained while others are reported to be doing it only to keep within state regulations. In any event, if we are to have new legislation, it is essential that the various states know what they are about and then, if possible, work for uniform regulations.

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Standard Practices for Rock-dusting

At a meeting of the American Engineering Standards Committee in New York on Dec. 11, 1924, the American Institute of Mining and Metallurgical Engineers was designated as sponsor for proposed American Standards in rock-dusting of bituminous coal mines. Howard N. Eavenson was appointed chairman of the Sectional Committee to prepare these standards and, on Jan. 22, 1925, a report was submitted to E. A. Holbrook, chairman of the Institutes Mining Standardization Correlating Committee.

Efficacy of Rock-dusting

When not less than a 50-50 mixture of rock dust and coal dust is thrown into suspension, the rock dust, together with the coal dust, absorbs heat and lowers the temperature of the flame of propagation below the ignition temperature of the coal dust. Further, the particles of rock dust get between the particles of coal dust and have a curtain-like effect. One of the most reasonable merits of rock-dusting is that once the dust is distributed systematically throughout a mine it remains there indefinitely and is always "on guard" during the dangerous period of the year (winter).

Beginning with 1910 and ending with 1924, there have been 58 explosions in which coal dust is known to have played an important part. There was a total loss of 2422 lives and of millions of dollars in property. It is estimated that 75 per cent. of the lives lost in these explosions would have been saved if the mines in which the explosions occurred had been systematically rock-dusted.

The Old Ben Coal Corpn. in southern Illinois operates twelve mines and began to install rock-dust barriers during the winter of 1917–18. Since that time there have been nine local gas ignitions in these mines and the management and men are certain that at least two of these explosions would have terminated in great disaster if it had not been for the rock dust. The flame was extinguished at the first barrier zone encountered, but the violence extended at least 3000 ft. beyond the zone in each instance.

Last November, a widespread coal-dust explosion occurred in the Rains mine near Rains, Utah. It is reported that about 1000 ft. of entry near the mine opening had been treated with rock dust and that the flame of propagation was "killed" when it entered this area.

On Dec. 5, 1924, a localized explosion took place in the Two Yard seam of the north district of the Llay Main colliery near Wrexham in north Wales, killing nine men; the lives of 415 additional workmen were saved by rock dust. It is reported that the range of the explosion was extraordinarily limited, the flame traveling less than 1000 ft. in any one direction from the point of ignition. Some of the survivors state that

they felt the propulsion of air and it was immediately followed by a cloud of mixed coal and rock dust.

Prevention of Formation of Fine Coal Dust

It should, of course, be definitely understood that rock-dusting is only an additional precaution and is not expected to take the place of any existing practice of keeping the mine well ventilated and as clean of coal dust as is possible. It may be desirable to "kill" the coal dust as it is in process of formation, or immediately after, particularly in dry and dusty mines. Some companies do this by using plenty of water at and near the working faces; for example, on machine cutter bars while undercutting in the immediate vicinity of the face before blasting, and on the broken coal before and while shoveling. On the other hand, some mining men believe that watering at the face is of no consequence as well as impracticable, and that sprinkling merely agitates the dry, fine dust. In the Pittsburgh bed, analysis of samples taken before and several months after washing down the gob, indicate that the dry fine dust before washing actually contained a greater amount of non-combustible matter.

The production and accumulation of fine dust can also be eliminated, in a large measure, at the working face by driving all workings on sight so that the minimum number of bumps will be left to be pick mined, by more careful handling of bug dust, by loading out all bug dust in the beds of cars, and by more efficient use of explosives. On haulage roads, the production of fine dust can be reduced by using tight-fitting, solid-body cars, by employing stiff hitchings, and by providing a well-constructed track. Some companies sprinkle loaded cars after they are loaded at the face, and also by sprays as trips are leaving inside switches or partings. The cost of drastic safety measures seems, on first thought, to be prohibitive, but our mines should be made safe and any expense in this connection can logically and fairly be charged to the consuming public.

Importance of Efficient Ventilation

Coal-mining men are now convinced of two important safety measures: permissible explosives and electric cap lamps. However, only 33 per cent. of the coal mined in 1923, when bituminous production was 545,000,000 tons, was shot by permissible explosives. The number of electric cap lamps in use at the present time is estimated at something over 200,000 and is growing. Rock-dusting and these other safety measures are very important, but it must not be overlooked that most mine explosions have had their beginning in gas accumulations, frequently originating in restricted areas at the working face, in abandoned areas, or at some other place where ventilation is not maintained as it should be. There must

not be too much "rule-of-thumb" relative to the volume of air required and constantly furnished at a given working face or in a given entry panel or other areas. The question uppermost is whether a sufficient quantity of pure air reaches every part of the mine, "brushes" all fresh working faces, and the shifting top in areas of pillar drawing. An accurate ventilating map and definite records of air at the face must be kept as well as water-gage and barometric observations.

Hazard Examination of Coal Mines

The Bureau of Mines seems to have established the fact that coal dust is dangerous as to flammability in proportion to its fineness and dryness, and to the proportion of volatile combustible matter to fixed carbon plus volatile combustible matter, as illustrated in the equation

$$\frac{\text{Volatile matter}}{\text{Fixed carbon} + \text{Volatile matter}}$$

This equation indicates that anthracite dust is practically non-explosive, for which reason rock-dusting is unnecessary in anthracite mines. Furthermore, bituminous dust larger than 20 mesh will scarcely enter into

Fig. 1.—Taking road sample before rock-dusting; note dark ribs and roof.

an explosion. Dust that is about 100 mesh is dangerous, especially if dry, and dust that passes 200 mesh and is dry must be classed as exceedingly flammable.

An examination for coal-dust hazard must be made by a competent safety engineer of each mine contemplating rock-dusting. Samples of the coal must be taken at different points in the mine, and of dust from the roads, ribs, roof, and timbers, in the approved manner, and sized and

analyzed. Likewise, the quantity of dangerous road, rib, roof, and timber dusts in a specific stretch of passageway must be calculated with a view to determining whether or not they should be cleaned before rock dust is applied, also the approximate amount of rock dust, by weight, that will be required to rock-dust properly a given length of passageway. It may be pointed out that accurate floor samples can only be secured by taking a groove to the solid; see Fig. 1. All records should be kept accurately and systematically. The following identification tag is used by the Pittsburgh Coal Co.

Form 4-4 SAMPLE IDENTIFICATION

Number.........

Mine.. ....19..

Kind of Sample.... ....

Material Applied.............................Lb. Applied........

Location..

....

Width of Channel......................Cross Section.............

Volumeter Reading................Per Cent Incombustible.........

Sampler...

Note.—Show whether before or after dusting for "Kind of Sample."

As a matter of interest, it might be stated that in examining the sizing and analysis records of a number of samples of dust collected in entries of dry and dusty mines in the Pittsburgh bed before rock-dusting

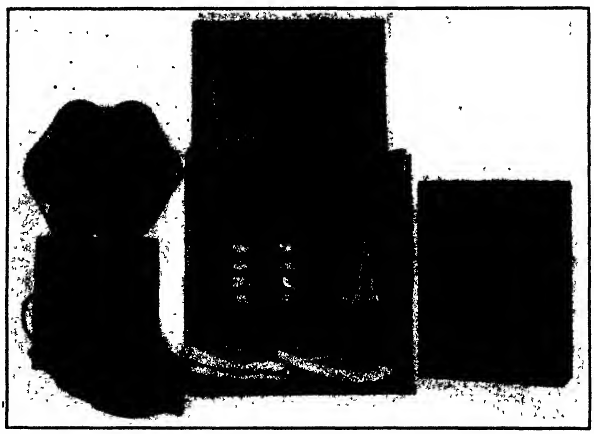

FIG. 2.—ROCK-DUST TESTING KIT.

was started, the average incombustible content of the haulage-road samples was 43.5 per cent., the range being between 27.2 and 54.6 per cent. The average incombustible content of the same number of rib, roof, and timber samples taken at the same points was 30.8 per cent., with a range of 20.7 and 50.1 per cent. The amount of 200-mesh dust contained in the road samples, all of which had passed a 20-mesh sieve, ranged from

17.4 to 27.0 per cent.; the amount of 200-mesh dust contained in the rib, roof, and timber samples, all of which passed a 20-mesh sieve, ranged from 54 to 65.3 per cent.

A rock-dust testing kit (Fig. 2) is now on the market with which it is possible to collect samples, to make size tests of coal dust and pulverized rock dust, and to make a rapid volumeter test for incombustible matter in coal and rock-dust mixtures. For convenience, it is assembled in two parts; one the sampling kit and the other the equipment necessary for sizing and testing. With a little study, any responsible man about a mine can use this kit. For all practical purposes, the carbon dioxide and inherent ash and moisture that may be in any particular coal can be ignored in preparing calibration curves.

Raw Materials for Rock Dust and Cost Thereof

Limestone is now used by seventeen companies, principally because coal men know little about pulverizing and all desired to make an early start in rock-dusting their mines. The dust used thus far ranges in fineness from 50 to 92 per cent., with an average of 74 per cent. through 200 mesh. It is fairly generally agreed that the most convenient dust to handle is about 60 per cent. through 200 mesh. Limestone dust can be purchased from numerous limestone companies, and is usually shipped in 80-lb. sacks, similar to flour and cement, which arrangement facilitates, handling and prevents loss. Sacked limestone dust, 50 to 60 per cent. through 200 mesh, can be purchased at Youngstown, Ohio. for $4.50 per ton, plus freight charges to the Pittsburgh district of $1.45 per ton, or a total of $5.95 per ton. Limestone dust, 75 per cent. of which will pass 200 mesh (and prepared for shipment in the same manner) can be purchased in Bellefonte, Pa., for $5 per ton. Transportation charges to the Pittsburgh district are $1.50 per ton, or a total of $6.50 per ton. Erie, Pa., sacked limestone dust, 60 per cent. of which passes 200 mesh, can be delivered in the Pittsburgh district for $5.95 per ton, and dust of which 80 per cent. will pass 200 mesh, at $6.45 per ton.

A number of the shale formations associated with the coal measures will contain less than the allowable amount of silica, combustible matter, and moisture, and will be suitable for rock-dusting. Some shales contain as low as 8 per cent. of free silica, while others run as high as 50 per cent. The average, however, for a large number of samples taken in various localities in the United States, is about 20 to 25 per cent. Twelve companies are already using shale and find it more economical to crush and pulverize the rock at the mine. Transportation charges, at least, are saved. It is doubtful whether pulverizing can be done efficiently underground, because of the moisture that prevails during the major part of the year. At one operation, where the pulverized dust is prepared on

the ground, it is claimed that it costs $1.75 per ton to deliver the rock to the crushing and pulverizing unit on the surface, and $1.25 for crushing and pulverizing, or a total of $3 per ton for the finished product. It might be added that the wage scale at this mine is on a basis of $7.50 for day labor. At another operation, it costs $1.91 per ton for crushing and pulverizing, which figure includes all legitimate charges.

Physiological Effect of Silica in Rock Dust

Physiological tests have shown that pure limestone dust is not injurious to health. Rock dust that does not contain more than 25 per cent.

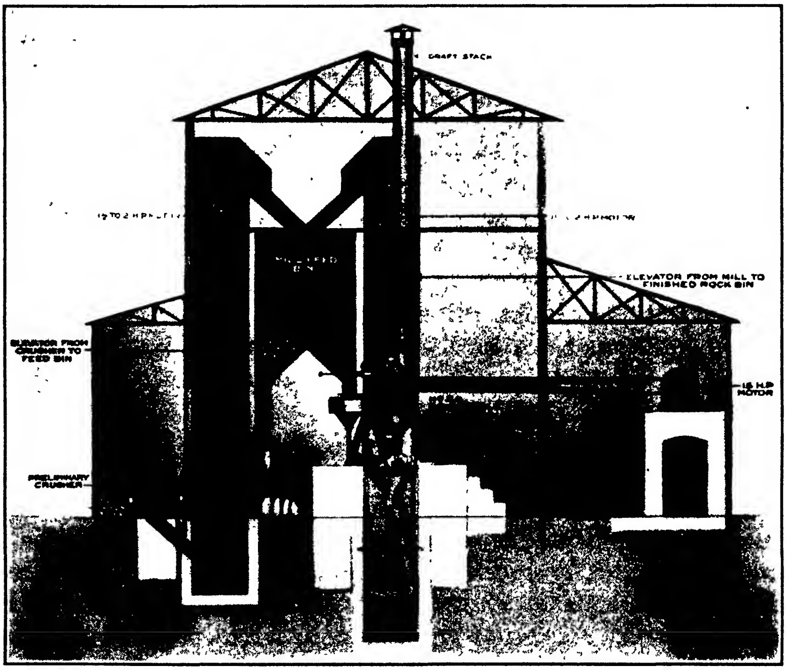

Fig. 3.—Rock-pulverizing unit with Griffin mill.

of free silica is not likely to be harmful. However, investigators are still in doubt as to whether the effect is really mechanical or toxic. This is, however, of minor importance when considering rock-dusting, for little rock dust is suspended in the air except during the actual operation of coating the passageways or preparing concentrated areas or leading barriers, and if warranted a standard respirator may be worn by the workman. The only other time that dust is really suspended in the air in appreciable quantity is when it is actually fulfilling the purpose for which it was intended. Rock dust containing as much as 35 per cent. of free silica has been used in some mines in Great Britain for a period of 12 years and no ill effect has been reported.

Pulverizers and Fineness of Rock Dust

There are on the market a number of crushing and pulverizing units that will effectively prepare dust for rock-dusting purposes. All the manufacturers make various claims for the efficiency and economical operation of their machines. So far only seven plants have been installed at mines, and there are no reliable data available on which to judge their relative merits. The Griffin mill (Fig. 3) will pulverize dust, depending on the screens employed, to any size up to and including 75 per cent. through 200 mesh. This mill actually makes a finished product in one operation without the use of auxiliary screens or other separating apparatus. The manufacturers of this will claim that 90 per cent. of all the pulverizing equipment used in Great Britain for rock-dusting purposes is of this type. Other types of well-known machines that are being used for pulverizing rock are the Apco and Raymond.

It is improbable that a mechanical dryer will have to be employed in connection with a crushing and pulverizing plant, provided that the raw material is stored in a dry place for a reasonable period.

Hygroscopicity of Rock Dust and Coal Dust

In addition to such considerations as percentage of free silica, combustible matter, and moisture, it would be ideal if the rock dust should dry out faster or at the same rate as coal dust. During the summer months, the mine will be much cooler than the ventilating air and moisture will be deposited all over the inside of the mine and, following the theory of the formation of rain drops, the fine rock dust is the first to attract the moisture. For obvious reasons, a dangerous condition will exist if in the autumn and winter the coal dust dries out faster than the rock dust. In so far as specifications are concerned, it is probable that the combustible content is of more importance than that of free silica. The relative specific gravity and specific heat of various raw materials are likewise unimportant. The fineness of the dust for various purposes and its physical properties are outstanding considerations. Possibly dust can be doctored or blended so that it will not take up water rapidly and will dry out consistently. Further research is being planned regarding these matters.

General Rock-dusting

About 85 per cent. of coal-dust explosions in America have originated on narrow work, either along the haulageways or at the faces of development workings. Rock-dusting should, therefore, be done first on all haulageways and other narrow work in use up to and including room necks, and up to within 40 ft. of the face or to the last break through of all development workings. Dusting should start at the face and proceed

toward the shaft or other openings, and preference should be given to the more gaseous sections. Some mining men believe that it will not be necessary to rock-dust unused back entries. No fine coal dust is "manufactured" in these entries, and furthermore no explosion will occur without a source of ignition, but some fine coal dust as well as rock dust is carried into these entries by the return air current. Others feel that rooms need not be dusted; but the coal-dust hazard exists in rooms, a source of ignition is possible and rock-dusting may eventually extend into these workings.

Rock-dusting consists of spreading a thin layer of dry rock dust on the surfaces of ribs, roof, and timber. For initial dusting, depending on conditions, 2 to 6 lb. is used per linear foot. It may or may not be necessary, depending on sizing and analysis records, to apply much rock dust directly on the floor. The roadways, depending on roof conditions and grades, may contain a relatively high percentage of incombustible material, and some dust always falls off the ribs during dusting and settles on the floor. In other cases the road dust may contain proportionately a greater percentage of combustible. Fine coal dust settling on the rock-dust coating will stick to the rock dust, and will not run off and fall to the floor as was originally expected. Another theory that is pretty well "blasted" is that the ventilating current can be depended on to distribute rock dust effectively to any great extent. It takes weeks under normal conditions for any appreciable quantity of coal dust to settle on rib, roof, and timber. If rock dust is blown into a ventilating current, the major part of the dust is deposited in the passageway, particularly on the floor in the first 200 ft. It is only the very fine, microscopic dust that is carried along in the air current and finally deposits on the floor, rib, roof, and timber. Some of the finest dust may be carried out of the mine by the ventilating current.

Record of Dusted Workings Should Be Kept

A permanent record of rock-dusting must be kept. This should show all the entries of the mine, when they were rock-dusted, weight in pounds and kind of dust used, date of sampling, and results of analysis. One page of the record book should be used for each entry, and should be posted weekly from the daily rock-dusting reports. A mine map of small scale should be prepared indicating all rock-dusted areas, as well as barriers, rock-dust zones, etc. The path to safety is not easy and rock-dusting will fail just as sprinkling failed in several well-known instances, if it is not applied effectively.

Distribution of Rock Dust

Several companies in western Pennsylvania have started applying rock dust by the hand method, as in Great Britain. In one mine five men

dusted 2100 ft. of entry per 8-hr. shift at a cost of about 2.5 cents per linear foot. Costs by the hand method in Illinois have been as high as 5 cents per linear foot. Hand dusting is better than no dusting and may be an excellent way to make a start. However, sooner or later it will be replaced by a more economical method. In hand dusting, the workmen are exposed to a certain amount of dust, and it is impossible to apply a uniform coating of dust to the surfaces being treated, although the coating may be thicker.

Dusting Machines

The country is full of ingenious dusting machines, but most of them are not perfected, consequently they are inefficient and not economical. Nevertheless, all of them have done their duty in helping the cause, and

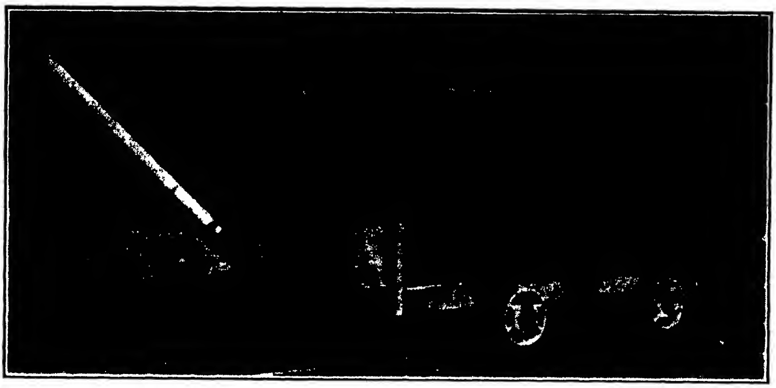

Fig. 4.—Rock-dust distributor developed by Inland Collieries Co.

some will survive while other new designs will be built. In any event the designers and mining companies concerned are to be praised for their initiative and resourcefulness. The principle of some machines is based on the injector and compressed air or blower, others use a blower, the dust in some cases being fed into the air current outby the fan, while in others it is introduced into the fan intake air. One company has designed a combined pulverizing and distributing unit. Some employ stationary nozzles while on other machines the nozzles are flexible. In some cases the dust is mixed with water and applied in a wet condition; in one case the workings are first wet down with water and then dust is applied by a blower. These two latter methods are very unsatisfactory and cannot be called "rock-dusting."

The direct dry method of applying the dust with a low-pressure distributor is most sound in principle. This can be accomplished by either a fixed or hand-operated flexible nozzle. Most of the distributors now in use are of the low-pressure, flexible-nozzle type. A rock-dusting

unit may be transported by a mine locomotive or it may be self-propelling; in any event it is not likely that a large-scale machine will ever be operated by one man.

One of the best-known dusting machines at the present time is that designed by the Inland Collieries Co., Indianola, Pa.; see Fig. 4. This is of the flexible-nozzle type, which is also the type employed by the Old Ben Coal Corpn. in Illinois. Another distributor, of the fixed-nozzle type, which works efficiently, is that recently designed by the Pittsburgh Coal Co.; see Fig. 5. The Miller machine, as modified by the Consumers Mining Co., Harmarville, Pa., is also of the fixed-nozzle type. Two men with any one of these units can lay a uniform coating of dust on the floor, rib, roof and timbers, over a distance of about 1 mile in an 8-hr. shift.

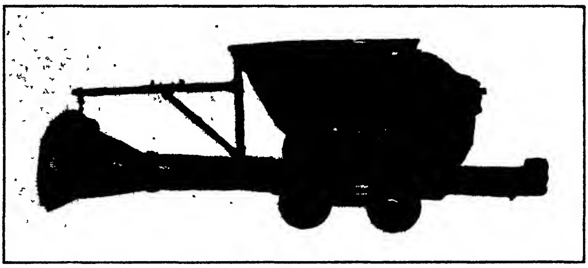

FIG. 5.—ROCK-DUST DISTRIBUTOR DEVELOPED BY PITTSBURGH COAL CO.

Flexible and fixed nozzles, like everything else, have their advantages and disadvantages, and experience will decide their relative merits. While numerous types of dusting machines can be devised, it will cost considerable money to develop any particular type into an efficient apparatus. Rock dust is a difficult material to handle because of its relatively high specific gravity, high angle of repose, and tendency to pack. The smaller and independent companies, at least, will, no doubt, find it more satisfactory to buy one of the distributors on the market, the efficiency of which has been demonstrated.

In ventilating currents of less than 500 ft. per min. it is especially desirable that the distributor travel against the air current in order to protect the workmen better. In the case of a flexible nozzle, this procedure will aid closer inspection.

CONTAMINATION OF ROCK-DUSTED AREAS

It has been found that most distributors actually waste dust in that they apply it too thick and not uniformly. This, of course, is due in a measure to the inexperience of the operator; but it is of the utmost importance that the feed mechanism of the distributor be reliable so that a uniform coating can be applied economically. Samples of dust from ribs, roof, and timbers taken after rock-dusting usually contain 75 per cent. of

incombustible, and often 90 per cent.; see Fig. 6. On first thought, this may be considered an advantage, but the rock-dust coating in time becomes contaminated by various agencies, and it is desirable to apply new dust from time to time as warranted. It is fairly well understood that rock-dusting will be required at least twice each year; once in the early autumn as the mine dries out, and again about the first of the new year (mid-winter). However, careful inspection and sampling will

Fig. 6.—Taking rib, roof, and timber sample after rock-dusting; note increased illumination.

determine when redusting is necessary. Certain stretches of haulage roads where an excess of dangerous dust is made and deposited each day may warrant redusting semimonthly. Haulageways should always be cleaned up prior to dusting operations.

Cost of Rock-dusting

Minimum cost can only be realized by systematic dusting with an efficient distributor after a due amount of experience. Few reliable cost data are available, and the range of variation is so great that even wide generalizations are likely to be unsatisfactory. The most desirable figures will be unit costs per ton of coal mined and on a long-term basis. The mines in which rock-dusting is being done have worked rather irregularly during the past year, consequently the best cost figures available are on a basis of linear feet of entry. These figures average about 1 cent per linear foot of entry; two companies assert that the cost in their mines on a tonnage basis is about ¼ cent per ton of coal mined. It must be remembered that, as in the case of all other reliable cost data, the cost of rock-dusting must account for many items of expense and not merely the cost of labor and dust. It is true that the cost of cleaning up haulageways prior to rock-dusting ranges from 5 to 8 cents per linear foot, but this item cannot be considered a legitimate rock-dusting expense.

In the mines of one company, two men are now rock-dusting over 6000 ft. of entry in an 8-hr. shift or in 4 hr. of actual dusting, and it is reasonable to expect that eventually it will be possible to dust effect'vely 2 miles of entry in 8 hr. Furthermore, the cost on a long-term basis should not exceed ½ cent per ton of coal mined.

Rock-Dusting Reports

Proper and accurate data should be kept on printed blanks supplied to those in charge of rock-dusting undergrounds. Samples of such forms are shown by the three following blanks of the Pittsburgh Coal. Co. and Inland Collieries Co.:

Pittsburgh Coal Company

Daily Stone-dusting Report

................................Mine ....19....

Entry No.	Average Cross Section	No. Feet Cleaned Up	Time Cleaning Up			No. Ft. Applied	Time Applying			Lb. of Stone Dust Used
			No. Men	No. Days	Rate		No. Men	No. Days	Rate	
Totals										

Show delays on bottom lines of report. Report Made By

....

Fig. 7.

PITTSBURGH COAL COMPANY

MONTHLY REPORT OF STONE-DUSTING

....—............................Mine Month Ending.................

Date	Total Lineal Feet Applied	Average Cross Section	Pounds of Stone Dust Used	Lb. of Stone Dust Per Lin. Foot	Cost of Cleaning Up	Cost of Applying Stone Dust	Cost of Stone Dust Used See(*)	Total Cost	Cost Per Lineal Foot	Daily Tonnage	Cost Per Ton
Aver.											

Inventory of Stone Dust				Record of Samples Taken			
Items	Amount (in Pounds)	Invoice Cost (Include Freight)	Unloading and Storing	Date	By Whom Collected	Per Cent. of Incombustible	
						Bottom	Roof and Sides
On hand first of month Received during month Total Used during month On hand at end of month							
Average "cost per lb." used in computing this report $.. Report completed by .... Approved .... Superintendent							

FIG. 8.

INLAND COLLIERIES COMPANY

ROCK-DUSTING REPORT

Date.................... ....

Place	Time in Min.	Dust Used, Lb.	Stations		Distance Dusted, Feet	Lb. Per Lin. Ft.	Cross Section of Place	Oz. Dust Per Cu. Ft.	Kind of Dust	Remarks
			Start	Stop						
Totals										

			No.	Rate	Amt.	Names
Lb. of dust on car beginning shift		Dust Man				
Lb. of dust on car end of shift		Motorman				
Lb. of dust on supply car beginning shift		Extra man				
Lb. of dust on supply car end of shift		Total				
Lb. of dust taken in mine today						

FIG. 9.

ROCK-DUST BARRIERS

Rock-dust barriers, or heavy concentration of rock dust called "zones," at desirable points may be used to advantage, but they are usually considered as secondary defenses. The so-called "box" and "concentrated" types may be employed to isolate old abandoned workings, panels, live sections of a mine, splits, and at other key positions, as well as in the passageway between two connecting mines. They may hold from 1 to 3 tons of dust; in other words, they should contain 100 lb. of dust per sq. ft. of cross-sectional area at the point of installation. They are installed against the roof or in an excavation made in the roof, and should extend across the entry. The cost of box barriers, installed, is estimated at $75 each; concentrated barriers will cost, installed, about $150 each. The V or "trough" type contains from 100 to 200 lb. of dust, and may be installed in batteries of 15 or more in strategic positions or restricted points such as sharp bends in entries, on the inby and outby sides of overcasts, etc. They may or may not extend across the entry, depending on their use and position. Trough barriers, installed, will cost

about $2.50 each, or about $37.50 for a battery of 15 troughs. All barriers should be constructed so that they will be operated by the advanced wave of an explosion in either direction, and will remain in operation during a period of at least 7 sec. The dust falling as a curtain is whirled into suspension and dampens or blankets the flame. The cost of barriers cannot be prohibitive, at the same time they should fulfill the specifications proposed by the Bureau of Mines. A great assortment of barriers is now in use, principally in the Rocky Mountain states. One type of V, or trough barrier made of lead-covered sheet steel, to prevent corrosion, is now on the market.

No practical, mechanical method has been devised so far for dusting back or trackless entries. Dusting such passageways by inserting a pipe through the stopping at certain points is not a success, as ventilation cannot be controlled so as to deposit the dust evenly. The air travels either too slowly to carry the weight of the dust or too rapidly to deposit it effectively. It is possible that the barrier, or zone, or in fact the hand-dusting method, as practiced in Great Britain, may be the final solution of this problem.

Other Advantages of Rock Dust

Rock-dusting Increases Illumination Underground

About 90 per cent. of the light underground is absorbed by the coal. The rock dust, and particularly that prepared from limestone, greatly increases the illumination and, consequently, increases the efficiency of the workman and decreases accidents. One company is installing a crushing and pulverizing unit and will prepare dust from shale made in the mining operation for dusting back entries and for barriers, if such are ever employed. However, this same company will purchase crushed limestone, pulverize it at the mine, and use it on all main haulageways, claiming that the motormen are enthusiastic over the results of the increased illumination. It is also possible that limestone dust will protect steel timber, prevent spalling of roof and coal, and in a measure neutralize acid mine water.

Rock Dust as Fire-fighting Material

Rock dust may be an efficient fire-fighting material and is, no doubt, much safer to use than either water or chemicals. It is reported that a terrific fire in dry coal in one of the mines of the Old Ben Coal Corpn. was successfully extinguished by the use of rock dust. The attack really started about 100 ft. from the fire on the intake, and consisted of throwing dust from the troughs toward the fire. As reported, the great cloud of rock dust seemed to cool the area so that advance could be made and additional dust introduced. Propping, of course, was done as the

advance was made. The dust sealed the fire, except in large crevices and in spots along the ribs. A second crew filled these crevices with shale dust and spread more dust along the rib where warranted. In a short time the fire area, which was about 100 ft. long and 12 ft. wide, was completely covered with several inches of dust. The remains of the fire and the coal, which was hot or warm, was then loaded out in the usual manner.

Several mines in Illinois keep on hand, at desirable points, sacked rock dust for fire-fighting purposes.

Rock Dust as Stemming Material

Rock dust may have special merit as stemming material for shot-holes, as compared with clay or other inert substances. It is claimed that the percentage of lump coal can be increased, with a reduction in consumption of explosives, but no actual quantitative tests have been made so far. "Cushioned" blasting has been practiced by a few expert shotfirers, and its advantages have been recognized in connection with the use of permissible explosives. Stemming consisting of loose rock dust will produce a cushioned effect. The procedure, in brief, consists in placing one or more cartridges of rock dust in the hole on top of the explosive charge. The explosive cartridges, or the cartridges of rock dust, are not slit. About 1 ft. of solid tamping is usually placed at the end of the dust charge or the collar of the hole. The explosion is supposed to compress the rock dust and wedge it tightly in the mouth of the hole, so that none of the gases can escape until they do their work in bringing down the coal. If this is true, there is no energy left to distribute the dust into the room. Some mining men believe that the force of the explosion really compresses the first rock-dust cartridge, completely blocking the hole at this point and does not affect the remaining cartridges. In either case, it is a question as to how well the gaseous products of combustion of a properly made shot aerate and distribute the rock dust. In the case of a blown-out shot, however, the rock-dust stemming may help to quench the flame. It is also doubted whether sufficient dust will be employed as stemming material to rock-dust a room effectively as advance is made, but at one mine where experiments were made with rock-dust stemming, it was found that the dust was distributed in the room as far as 50 ft. back from the face. At this same mine a band of bone occurs in the middle of the bed, and it is important that this bone is not pulverized by the explosive charge. The officials of this mine believe that more lump coal and cleaner coal is produced with 20 to 30 per cent. less explosive. It is possible that this increase in lump coal and reduction in amount of explosive is due more largely to part "air-spacing," closer supervision, and more accurately placed and drilled holes. In any event, if rock-dust stemming will make it more easy to secure a

better "spreading" effect with permissible explosives than is usually obtained, the matter should certainly be given careful consideration.

Coöperative Research Work in Rock-dusting

The United States Bureau of Mines, under the immediate direction of George S. Rice and J. W. Paul, has led the way in investigating the theories of mine explosions and methods of their prevention. Many mining companies, as well as manufacturers of safety appliances, are now studying the practical phases of rock-dusting, and all are contributing valuable information on the subject. Rock-dusting has developed into a real engineering problem and, as usual, many theories are giving way to the practical.

Coöperative research work relative to rock-dusting is being carried on by the Bureau of Mines, Carnegie Institute of Technology, and the Advisory Board of Mine Operators and Engineers of Western Pennsylvania. One problem concerns a more satisfactory quantitative analysis for free silica, and the determination of the shale formation associated with the principal coal measures of the country that may be suitable for rock-dusting purposes. A second problem concerns a collection of data relating to costs, equipment, and systematic methods of treatment. Still a third problem has to do with a field study of the relative efficiency of rock dust as a stemming material. A bulletin covering the results of these investigations will be ready for distribution early in the fall of 1925. It might be added that an additional problem regarding the effect of fineness and nature of material on its efficiency for rock-dusting has been proposed for the year 1925–26.

Conclusions

Rock-dusting is the most reliable, as well as the cheapest, method known at present to prevent and limit coal-dust explosions. However, it cannot be handled in a haphazard manner and, like all safety measures, must be done thoroughly to be effective. Likewise, as in the case of other safety measures, it must be considered as simply an extra precaution. Furthermore, it is well to emphasize the fact that rock dust alone will not make our bituminous mines entirely safe. Fine, dry, coal dust can be "killed" as it is made, and its accumulation in dangerous quantities can be prevented. It is also imperative that we take advantage of "approved" equipment and appliances and permissible explosives. Last, but not least, we must properly and conscientiously inspect and ventilate our mines and, thereby, prevent an accumulation of gas, which is the common source of ignition for coal-dust explosions. In conclusion, it may be stated that while there is much to be learned regarding both

methods and costs, there is no apparent reason whatsoever for delaying the application of rock-dusting in our bituminous coal mines and thus making them safe.

Acknowledgments

The writer is indebted to the following members of the staff of the Bureau of Mines: J. W. Paul, W. A. Selvig, C. W. Owings, and M. W. von Bernewitz; also to C. H. Dodge, research fellow Carnegie Institute of Technology, and to J. T. Ryan, of the Mine Safety Appliances Co., Pittsburgh, Pa., who reviewed and criticized this report. Most of the photographs were supplied by the M. S. A. Co., which marketed the first complete line of rock-dusting and testing appliances.

DISCUSSION

H. W. Hardinge, New York, N. Y.—There is a coal-dusting apparatus that combines the grinding and distributing at the same time; it is on a car together with a 500-lb. bin. The blowing unit may be equipped with long pipes so that the dust can be transmitted through various passageways. In this system, the rock, which may be obtained from the mine itself, is dumped into the hopper and the mill grinds the material, stirs it, and distributes it very uniformly. This eliminates the necessity of grinding above ground, and then distributing below ground. The entire operation is confined to one unit, which should eliminate considerable labor. This unit embodies a new reverse-current air classification, taking advantage of normal atmospheric pressure being introduced into the partial vacuum produced by the suction fan, and at the same time returning any oversize to the grinding mill, while putting the fine dust into circulation the moment it is produced.

George S. Rice, Washington, D. C.—The author uses the figure that the Bureau of Mines in its experiments decided was the right amount for barriers; namely, 100 lb. per sq. ft. of section. But he says that from 1 to 3 tons should be put on the barriers. Almost any entry will have a cross-section of 50 sq. ft. so that a barrier must have at least 2½ tons, which I think should be the minimum.

At the start of the experiments, we used too little dust in the various trial barriers and found that 100 lb. per sq. ft. is required to insure filling the air of the entry with rock dust in sufficient cloud density to separate the coal-dust particles and to cool the flame by the absorption of heat. Only a part of the loading is brought into action but the surplus is necessary to provide that portion.

One of the large mining companies questions the utility of rock-dust barriers, claiming that they will be operated after the explosion has occurred. There was a misconception of how they operate. This is

effected by the wave of air which precedes a dust explosion and makes it possible.

The author speaks of a certain machine that will dust by a wet process. It is no longer "dust" if it is wet, but that machine may serve a very useful purpose. I observed one in use in Utah and noted that if the coal ribs are more or less cracked and creviced, the mud will fill the cracks, after they have been cleaned of coal dust, then less dry rock dust is required afterwards. There appears to be merit in that combination. The subsequent test will be whether the dry loose dust on the surface of the caked dust has sufficient percentage of combustible to propagate an explosion. Some of the companies in the West think that filling these cracks greatly retards the weathering of the coal. The plan might be found beneficial in the Pocahontas W. Va., mines to deal with their columnar friable coal ribs.

The Bureau of Mines is not attempting to determine the superiority of one dusting machine over another. We are glad to see the tremendous interest in the development of these numerous types. At present, the method of operating is to drive these machines directly from the trolley wire, using open motors. I believe the time will come when dusting machines will be operated from storage-battery locomotives of the permissible type, and will have permissible motors to drive the fan for distributing the dust. Then they can be used in entries from which the trolley is excluded because of the possibilities of firedamp.

Coal-dust explosions are not easy to make and therein is the danger at the present time. The combination does not occur once in a million times; but it may occur any time where sufficient precautions are not taken. Some of our large railroads carry millions of passengers for years without accidents to passengers, but that does not cause them to stop looking after the tracks; they have daily inspections. They have to guard against the remote possibility of a wreck. Similarly, in coal mining, we must guard against the rare possibility of explosions by the utmost unceasing vigilance.

THOMAS G. FEAR, Indianola, Pa. (written discussion).—Under the heading of Cost of Rock Dusting, the author states that, "The most desirable figures will be the unit costs per ton of coal mined." This cost per ton of coal will not reflect the actual cost of rock dusting as accurately as the unit cost per linear foot of entry. Rock-dusting in one mine, where the coal seam is thick, may be carried on inefficiently and still show a lower cost of rock dust per ton of coal mined than at another mine where a comparatively thin seam is worked and rock dusting is done efficiently. This is due to the fact that more headings are required in the thin seam to produce a certain tonnage of coal.

Under the heading of Rock Dust as Stemming Material, the author condemns rock-dust stemming material because he believes that it is of no added advantage commercially, while his paper was written on safety in coal mines. He states that no actual quantitative tests have been made so far. One mine in Illinois used rock dust as stemming material for one month and increased the percentage of lump coal 9 per cent. Rock-dust stemming properly done does produce a greater percentage of lump coal than the ordinary solid clay tamping, less explosive is required per ton of coal, and there is a reduction of the amount of powder smoke after the shot. The introduction of 520 lb. of rock dust in every 250-ft. room is bound to decrease the coal-dust hazard, which is on everybody's mind at the present time.

EDWARD STEIDLE (author's reply to discussion).—The views expressed regarding the most desirable unit costs of rock-dusting are to the point and should be considered by coal-mining men. Relative to rock dust as a stemming material, I merely presented an impartial discussion of the leading questions in connection with this subject. Mr. Fear indicated that a mine in Illinois has made a quantitative test, using rock dust as a stemming material; I would like to have more details regarding this example, because I have been unable to find a company that has actually made systematic quantitative tests. The Carnegie Institute of Technology, the Bureau of Mines, and the Advisory Board of Mine Operators and Engineers of Western Pennsylvania are carrying on, this college year, a coöperative research fellowship problem having to do with efficiency in blasting of coal. During March and April, quantitative tests using rock dust as a stemming material will be made and the results of the investigation will be printed in bulletin form for distribution about next September.

Value of Humidifying Methods in Explosion Prevention in Coal Mines

By D. Harrington, Salt Lake City, Utah

(New York Meeting, 1925)

During the past few years, there has been a trend toward the use of rock-dusting, rather than relying on humidifying, or the use of water, to limit or prevent explosions in the coal mines of the United States. This is partly because British coal mines have adopted rock-dusting and, at least in a sense, have condemned the use of water. Moreover, during the past few years, particularly in the latter part of 1922 and in 1923 and 1924, several explosions with heavy loss of life occurred in coal mines of the United States that were known to have more or less extended sprinkling, or humidifying, systems.

The sentiment created by these disasters quickly caused a distrust of explosion-prevention methods requiring use of water and simultaneously caused more or less of a stampede into rock-dusting. Much of the wholesale condemnation of watering methods was without adequate knowledge, or at least without adequate consideration, of local conditions in each case, and rock-dusting was adopted largely without sufficient knowledge of how to rock dust safely or correctly. However, mines that had been using watering methods and had suffered these recent serious disasters (notably Dolomite, Dawson, and Castle Gate) instead of abandoning the use of water when operations were resumed after the disaster, greatly extended their watering systems. At the same time they took other precautions as to electricity, ventilation, blasting, etc., and supplemented the watering system with rock-dusting where the latter was likely to be the more effective. The trend toward rock-dusting during the past year or two (succeeding the recent mine disasters) is very similar to the rapid movement toward watering, or humidifying, methods, about 1910 to 1912, after a series of disastrous mine explosions.

The Phelps-Dodge Corpn., which operates a large property at Dawson, N. M., after an explosion in its No. 1 mine in February, 1923, decided that it is dangerous to have all its "explosion-prevention eggs in one basket" and so adopted what may now be termed the Western coal-mine explosion-prevention system, in which both rock-dusting and watering are used, supplemented by other up-to-date mining methods and practices; such as exclusive use of modern electric safety lamps, with magnetically locked flame safety lamps for testing purposes; use of

permissible explosive exclusively; use of electric shot-firing after the shift has left the mine; division of property into absolutely separated units, each ventilated by itself and each having fewer than 250 men; use of permissible electrical equipment exclusively in so far as such equipment is available, etc. The Dawson installation utilizes rock dust on all intake haulageways as far into the mine as freezing extends in the coldest weather; beyond this point watering methods are used. Every working place is piped with water and at each face there is sufficient water hose to allow of wetting the entire face region (roof, ribs, floor, coal pile, gob pile) by the face worker, who is required to do this several times per day, as well as to wet down the top of all loaded cars before they leave the face. In addition, machine runners are required to use a water spray on all mining machines in such manner as to wet thoroughly the "bug dust" as it is made. Sufficient "day-pay" sprinklers are kept continually sprinkling the open available dry workings (haulage roads, back entries, non-working pillars, etc.) so that they are not damp but actually wet (roof, ribs, and floor). In addition, the various panels of the mine are protected by over 100 well-placed, well-filled, rock-dust barriers. After the installation of these methods, Dawson became the Mecca of Western coal-mining men, with the result that the Western idea as to explosion prevention is that neither rock-dusting nor watering is the panacea, but rather that the use of water at and around the faces will kill the dust as it is being formed and that rock-dusting of haulage roads, supplemented by systematically placed rock-dust barriers, will protect the other parts of the mine.

The worst sufferer from the mine disasters in the United States, in 1923 and 1924, was the Rocky Mountain region, especially New Mexico, Wyoming, Utah and, to a less extent, Colorado; yet, there is no tendency to abandon the use of water in these states. The Phelps-Dodge Corpn., the largest producer of coal in New Mexico, in its Rules and Regulations, at Dawson, issued in 1923 says:

Firebosses shall be instructed to examine all places and report any accumulation of dust or where places are dry, such places shall be immediately posted with a danger sign and not allowed to work until brought into proper condition.

The new Utah State Regulations as to use of water are as follows:

Water on Mining Machines and Mechanical Loaders.—Coal-cutting machines and mechanical-loading machines shall not be operated in coal mines in Utah unless equipped with a supply of water applied in a manner to wet down and prevent the raising of fine coal dust into suspension in the air.

Sprinkling.—Every owner, agent, manager, or lessee of coal mines within the State of Utah shall provide and maintain water lines in all working places of sufficient size and pressure to furnish water in sufficient quantities for sprinkling purposes to wet down all coal dust that may arise and accumulate in and around working face. And each worker shall be kept supplied with a sufficient quantity of water

hose to enable all parts of the face region to be thoroughly sprinkled, this is to be used by the workers in each working place.

Men employed for sprinkling shall make a signed daily report, in a book kept for that purpose, of the sprinkling work done, condition of working places, pipe lines and any difficulty arising from the lack of pressure, pipe-line shortage, breakage, lack of hose, etc., this report to be countersigned by the mine foreman.

Men employed for sprinkling shall not be used on work other than sprinkling, without first having the permission of the superintendent of such transfer, it being understood that in case of such a transfer the vacancy shall be filled by a man qualified to do that work.

At Dawson and in Utah, dry coal dust is placed on essentially the same status as accumulations of methane. A study of the Dawson mine in January, 1924, showed that the firebosses could "post" very few, if any, places, as practically all open parts of the mines were being kept wet; except that the coal intake air courses, on which water could not be used because of freezing, were rock-dusted. At that time about 7 miles of this rock-dusting had been done. Before the Utah regulations were issued they were approved by every large producing company in the state.

In southern Colorado, in 1910–12, nearly 250 men were killed by a succession of gas-coal-dust explosions, and immediately thereafter extensive systems of preheating and water and steam-spray were installed, also some hose and water-car sprinkling. The result has been practically a cessation of explosions in the mines using this system; there has been but one such explosion, since 1912, involving death of about 20 miners, though there have been explosions in Colorado mines in which essentially no humidifying was done. That a person would have considerable difficulty convincing most of the old-time southern Colorado coal operators or safety men that humidifying methods are a failure is shown by the indifferent progress rock-dusting has made in Colorado, notwithstanding that the Delagua mine, about 20 miles from Trinidad, was probably the first fairly extensively rock-dusted mine in the United States.

While, in the spring of 1924, Utah took the lead among the mining states by making rock-dusting compulsory, a greatly extended use of water was also made compulsory. All mines are required to have water lines piped to all working faces and not only are "day-pay" sprinklers required to use water, but every miner must keep his working place sprinkled and every machine runner must use water on the cutting chain while cutting; and a determined effort is being made to enforce these requirements. While some mining men in Utah oppose the use of water partly on account of the cost, but largely because the wet slack is difficult to screen, hence greatly hampers sizing the coal, most of the companies, and especially the larger ones, go much farther with the use of water than the state regulations require. One mine manager, with much coal-mine operating experience throughout the

country and especially in the West, states that while rock-dusting will be done where required, he wants his mines kept "stinking wet;" and his wishes are being carried out. Another manager, also of varied experience, says that he is willing to experiment with rock dust but his mines are going to be kept wet. They even go so far in this mine as to sprinkle the floor of the workings that have been rock-dusted; curiously enough, the effect is good, as the rock-dust coal-dust mixture on ribs, roof, and floor seems to absorb and retain the moisture far better than does the mine dust when the rock dust is absent.

One of the unfortunate features in connection with Utah's effort to make its coal mines more safe and healthful is the fact that wetting the coal makes screening more difficult, so when consumers, particularly the large consumers, insist on better screening qualities, there is a tendency among some producers to limit the use of water, irrespective of its effect on the health or the safety of employees, or on the safety of the mine. When some producers do this, the producer who adheres to the spirit as well as the strict letter of law, loses business and is thus penalized for obeying the law and, also, for practicing sane safe mining.

In Wyoming, in many coal regions, water is scarce and the coal seems to be somewhat less explosive than in Utah, Colorado, and New Mexico; watering methods have been and are being used to only a limited extent, at least as compared with Utah coal mines. However, there appears to be a definite sentiment toward the adoption of state regulations in Wyoming, modeled largely after those in use in Utah; if this is done both rock-dusting (which is now being done to some extent) and watering will be in extensive use in Wyoming.

The foregoing shows that while the Rocky Mountains States are decidedly in favor of rock-dusting, they are by no means against watering methods; rather, they are extending the use of water as both a safety and a health measure. The mining men of these states realize that their conditions are such that unless all available precautions are taken, disaster is likely to follow; and these Western mines have problems that do not usually confront coal mines of other regions. In the East, during much of the spring, summer, and fall, the surface air is highly humid and higher in temperature than the mine workings; so on entering the mines the air currents deposit moisture, causing "sweating," thus tending to make fine dust in Eastern mines inert. About the only period of the year that these Eastern mines are dry is during a few winter months, and even then they have the advantage of the dust saturation throughout the workings during the six to nine preceding months. In the Rocky Mountain States, "sweating," as found in Eastern mines, is unknown and during all seasons of the year the surface air is decidedly dry, hence practically every cubic foot of air going through these Western mines abstracts, or tends to abstract, moisture from the coal and thus makes

the dust the more ready to explode. For instance, during the past summer at one Utah coal mine, the surface intake air entered the mine at 88° dry-bulb, 55° wet-bulb temperature, thus carrying about 2 gal. water per 100,000 cu. ft. of air; about 9000 ft. from the surface in this main air course, this intake air (about 50,000 cu. ft. per min.) had a temperature of 61° wet-bulb, 66° dry-bulb, hence was carrying about 9 gal. water per 100,000 cu. ft. of air. In this case the 9000 ft. of intake air course was being deprived of about 3½ gal. of water per minute or over 5000 gal. per 24-hr. day, amounting to over ½ gal. per ft. of intake entry per day. It is largely because of this situation that Western coal mines are made dangerous, that sprinkling fails locally, rock-dusting must be done on intake air courses, and watering in the interior of the mine.

Many Western coal mines are worked under 2000 ft. or more of cover, which tends to crush the coal or to cause "bumps," both conditions throwing much fine dust into the workings; also, many of the Western mines working in seams 10 to 30 ft. thick have roof and floor, as well as ribs, wholly of coal, hence the road or other dust in the mine runs 90 to 95 per cent. combustible instead of the 20 to 40 per cent. combustible road or rib dust found in many Eastern coal mines, where the seam is thin and roof and floor are of friable incombustible material, such as shale, slate, fireclay, etc. In these Western mines (with thick seams, ribs 10 to 20 ft. or more high, with roof, timber caps, etc. also that height, hence almost inaccessible for treatment or inspection) the opportunity for lodgment of the very fine, most dangerous dust, as well as of explosive gas is great and its removal or neutralization correspondingly difficult. Also many of the Rocky Mountain coals contain large amounts of more or less finely divided resin, which is extremely inflammable; many mines have oil seeps, which are dangerously inflammable in themselves and frequently carry explosive gases with gasoline or kerosene odor and probably much more sensitive to flame than methane. Some Western mines are decidedly gaseous; the Morley, Colo., mine has given off daily, for many years, over 2,000,000 cu. ft. of methane; in several mines 1,000,000 cu. ft. or more of methane is removed daily.

Laboratory tests of the explosibility of coals of the United States show that while, under standardized conditions as to coal-dust fineness and as to temperature of electric arc causing an explosion in the laboratory, Eastern bituminous coals gave pressures from 1 or 2 up to 15 lb. per sq. in., nearly every Western coal tested under similar conditions gave pressures in excess of 15 lb. per sq. in. and some of them gave pressures above 20 lb., or much higher than that shown by practically any Eastern coal. Similarly, Bureau of Mines *Bulletin* No. 167, page 344, shows that Western coals, in general, require a larger percentage

of incombustible (ash, shale, or other rock dust plus moisture) to prevent propagation of an explosion than do Eastern coals; the coal with the highest requirement mentioned in this series of experiments as to incombustible to prevent propagation of an explosion came from a southern Colorado coal mine. As in this case 82 per cent. of incombustible is necessary to prevent propagation of an explosion, whether sprinkling or rock-dusting is used, a dangerous condition can be averted only by the most constant vigilance.

When the Western operator considers the immense amount of dust unavoidably made as the result of local operating, climatic, stratigraphic, and other conditions, and the inflammability of the dust and of the gas found in his mines and that, unless the dust is mixed with about four times its own amount of very fine rock dust, he cannot prevent its propagating an explosion, he is naturally quite reluctant to rely on rock-dusting alone; also, as his faith in water methods alone is shaken, he is now inclined to think that his safety requires the use of both methods.

One of the most disastrous of the later Western coal-mine explosions (Dawson No. 1 Mine in New Mexico) was probably started by the ignition of extremely fine road dust that had settled on timbers, from the air on an intake haulage road; the dust had an incombustible content (rock dust plus moisture) of about 65 per cent. On the other hand when the practically pure coal dust of this property was mixed with 8 per cent. water and subjected to standard ignition tests (which ignite the dry dust at every attempt), the dust mixed with 8 per cent. water did not ignite; yet dry coal dust of the same size, when mixed with dry rock dust, making 58 per cent. incombustible, propagated an explosion readily. When there was practically 1 per cent. of methane in the air, an explosion was propagated through the dry dust when 66 per cent. incombustible was present. Inasmuch as very fine dry coal dust mixed with 65 per cent. incombustible ignited and started a disastrous explosion while the dust of the same mine when mixed with water so that 8 per cent. moisture was present would not ignite when subjected to a standard ignition test, it is natural to infer that, at least as far as ignition is concerned, moistening the dust is preferable to rock-dusting; and as undercutting, overcutting, shearing, drilling, shoveling, blasting, pillar pulling, etc. throw into the air much finely divided coal dust, it is readily apparent that around the face conditions are likely to be most dangerous. As flame for ignition is found most frequently at or around the face, from open lights and methane accumulations, or electric arcs and methane or dust or both, or blown-out shots and methane or dust, it is extremely desirable that the dust at or near the face be "killed" and kept "dead" at all times. As 65 per cent. incombustible will not prevent ignition of very fine Western coal-mine dust, and under some circumstances, such as the presence of 2 to 3 per cent. of methane, even 80 per cent. incombustible will fail to prevent

ignition, while 8 per cent. of water does prevent ignition, naturally it is deemed advisable (in fact, even necessary) to use water around working faces. The use of water at and around the face region, in addition to "killing" the dust, as far as aiding in ignition or propagation of an explosion is concerned, keeps out of the air the clouds of fine coal dust which are certainly detrimental to health of workers, particularly the machine runners. On the other hand, the omission of water at the face with the attempt to use rock-dusting, would tend to intensify the probable health hazard to workers from breathing dust suspended in the air; this is more true of the face region because air currents are likely to be inactive or practically non-existent at some faces, particularly those of rooms or pillars, and the very fine dust may remain suspended for hours to be breathed by workers.

Moreover, unless the dust is "wet down" at and around the face regions, fine dry coal dust from faces and from tops of or through openings in cars will soon settle upon adjacent rock-dusted surfaces, and the 15 to 30 per cent. of combustible that makes some of our coal-mine dusts inflammable will make rock-dusting ineffective almost as quickly as evaporation renders sprinkling ineffective. Recently a sample of very fine dust (both settled and rock-dusted) was collected from a rib of a dry main intake haulage road in a mine where water was used very sparingly at the face and not at all on top of cars; when allowed to sift over a lighted match, the resultant "flare up" was most indicative that rock-dusting, to prevent explosion ignition or propagation, must be renewed frequently when coal dust is not "killed" by water at the face region or elsewhere in the mine.

While the Rocky Mountain coal-mining region has greatly extended the use of water at and round the working faces, it has long been known that intake air courses, especially those acting as main haulage roads, have been most difficult to keep sufficiently moist. Recent explosions at Dolomite, Ala. and Dawson, N. M., originating comparatively near the mine entrance on the intake air courses of sprinkled mines have convinced many of the most enthusiastic advocates of watering methods that the use of water on these main haulage intakes is dangerous; in Colorado, though, the advocates of the preheating-humidifying system still maintain their position. In Utah, to a considerable extent in Wyoming and in New Mexico, and to a slight extent in Colorado, the plan now is to rock dust thoroughly the main intake haulage roads (roof, ribs, and floor), at least as far into the mine as freezing extends in winter; to divide the mines and have "day-pay" men sprinkle interior auxiliary haulage roads, room necks, and open accessible abandoned workings. In some instances, interior rope-haulage slopes are also being rock-dusted; in a few mines, some auxiliary entries are being rock-dusted; and in at least one mine, the Royal in southern Colorado, it is said that the rock-dusting is being

carried to the face and no water is used. In Utah, mines with a daily output of about 1500 tons now have three to five or more "day-pay" men whose sole duty is to sprinkle the interior workings (ribs, roof, and floor); in addition, some of these mines have sprays at main partings, which wet the top of all loaded cars as they leave the interior of the mine. The face workers are required to keep the face region wet down and open, non-working, but accessible, parts of some mines are kept wet by stationary water sprays.

One of the worst difficulties where main-haulage main-intake entries are rock-dusted is the coal spilled along the tracks from loose or open-type cars or from the high topping of cars, or both; this coal soon becomes fine and dry and when thrown into the air by passing cars, animals, and men, settles upon roof, walls, and floor and tends to make the rock-dusting unsafe in a short time. While the ultimate remedies for this would be the adoption of a tight car and the restriction of topping, neither remedy can be applied readily. In some Utah and Colorado mines, a water car is run along these haulage entries, keeping wet the region between and immediately outside of the track rails; meanwhile every feasible effort is used to prevent this spilling of coal and to do as much cleaning of the spilled coal as is feasible.

Failure to keep abandoned or non-working places well sprinkled is responsible for the extension of most of the explosions in mines where sprinkling systems are in use. These open non-working regions are very dangerous and, if they cannot be sealed, should be kept well sprinkled or well rock-dusted. Where they cannot be traveled, stationary water sprays running continuously are being much used in the West, but the safest method is to seal where feasible; the stationary sprays do good work when actually operating, but unless given fairly frequent supervision they clog and become inoperative.

While it is stated that practically 30 per cent. of water must be present to prevent propagation of a violent explosion through fine coal dust, the writer is somewhat disinclined to accept this. He has seen "bug dust" cut with water on the cutter bar that was so wet as to be almost "sopping," yet on analysis it gave but 12 per cent. moisture. Certainly no explosion, irrespective of its violence, if confined to the usual duration of but a fraction of a second, could get this material into such condition that it would ignite or explode in that short period of time. While the writer is skeptical that an explosion will get any support from coal dust with over 10 per cent. of mechanically mixed, or soaked, moisture, dusts of lignitic coals with 16 to 20 per cent. or more of combined moisture most certainly do ignite. It is possible, however, that a violent explosion coming from a dry region, and carrying much dry dust with it, may pass through a region of limited distance with wet "dust" on floor, ribs, and roof, and if fed dry dust or methane on the far side of the limited wet zone

may again take up fuel and continue on its way. However, the writer has seen where a 400-ft. zone of water drippers stopped an explosion absolutely from going into an entry, which was dry and dusty on the interior and from which a considerable number of men later came out alive; the explosion, stopped from going in one direction by these water drippers, went several thousand feet in another direction where there were no drippers and in its travel killed a number of men.

It is frequently stated that fine dry coal dust either will not mix with or absorb water or will do it only with difficulty or delay. Years of experience in Western mines prove that even in those mines that have no shale, slate, etc. admixture to aid in absorption of moisture and where the coal is of a more or less oily nature (oil actually bubbling out of the coal floor or roof in places) if the underground workings are sprinkled systematically, the territory not being allowed to become "bone" dry before given another supply of moisture, even the newly deposited very fine dry dust is easily moistened. However, where sprinkling is of a haphazard nature and successive applications of water made only after the workings have become dangerously dry, it is difficult to get fine dry coal dust moistened; in many cases it will float absolutely dry for days, even weeks, upon a pool of water.

One of the greatest fallacies in connection with the use of water in coal mines is that a mine is sprinkled when a water car or hose is run over a few workings once each week, month, or year and a little water is placed between the rails on the floor. Real sprinkling requires that ribs, timbers, and floor be thoroughly washed down and never allowed to become dry. If this is not done a mine is not sprinkled; if it is done, the ribs, roof and timbers will be kept free of dust and the floor will have the very fine, hence dangerous, dust either washed down under the coarse coal to the solid floor, or attached to larger pieces in such manner that only a violent explosion can bring it into suspension even if it should become dry. A sample of floor dust taken across the width of an entry in a 6-in. groove about 1 in. deep, where no sprinkling was done, gave 31 per cent. through 200 mesh, while a sample taken in the same mine (Dawson, N. M.) in a nearby place kept fairly well sprinkled gave but 11 per cent. through 200 mesh; at time of sampling, both places were fairly dry but the place with but 11 per cent. through 200 mesh had usually been kept well sprinkled. This is typical of the coarseness of the exposed floor dust where real sprinkling is done.

Another fallacy as to effective use of water is that when water is placed on roof, ribs, or floor, there is resultant damage from caving, sloughing, squeezing, etc. While probably at first there will be some falls or similar temporary trouble, and possibly in a few isolated cases permanent difficulties, the number of localities where permanent injury is suffered are very few. In many cases when operators had firmly

believed that great damage would be done if water was applied to ribs, roof, or floor, when forced by some emergency to try wetting, the danger failed to materialize. Eastern operators who have sloughing of roof or ribs, as the result of alternate "sweating" and drying, would in many instances eliminate this difficulty by using effective watering methods in the dry seasons in places where water will not freeze.

While it is interesting to read of explosions being stopped by rock-dusting and rock-dust barriers in southern Illinois, it is dangerous to generalize from this that similar results can be obtained in all coal mines. Illinois coal dusts are not nearly as inflammable as are coal dusts from many other parts of the country, particularly the Rocky Mountain States. The writer has seen a report of an explosion in a southern Illinois coal mine that was started by gas ignition by open lamp that blew out a number of brattices and stopped of itself, as there were no sprinkling, rock-dusting, or other explosion-prevention measures. The report stated that there was present "ample dry coal dust along the roads and ribs to propagate an extremely violent explosion." From this occurrence, it would appear that rock-dusting methods that would easily stop incipient explosions in southern Illinois would be of little utility in regions that have really dangerous dust.

While sprinkling is alleged to have failed in several instances, in practically every such case lapses from efficient sprinkling practice caused the trouble, rather than failure of the methods. The Dawson No. 1 explosion in February, 1923, and the Dolomite explosion in November, 1922, proved that it is difficult, almost impossible, to apply sprinkling methods safely or successfully to main intake air courses, especially those that act also as main haulage roads. This fact is being accepted by even the most enthusiastic advocates of watering methods, except possibly southern Colorado mines that use preheating and spray systems. The Dolomite explosion, frequently pointed out as a failure of sprinkling, really shows how advantageous sprinkling is, for the explosion, starting near the mouth of the intake haulageway, reached into the mine only about 1000 ft.; it killed about 90 men, who happened to be concentrated in a limited area, yet on account of the effectiveness of the sprinkling in this very dry mine, the explosion was unable to get into the interior of the mine where several hundred other men were employed. These men undoubtedly owed their lives to sprinkling. In a recent mine explosion at Kemmerer, Wyo., the flame was unable to penetrate a zone of a few hundred feet of water drippers and a number of men back of these drippers came out alive while the flame traveled nearly all ways from, but not through, those drippers with large death toll. In one well-sprinkled Western mine, Somerset, Colo., having much gas, a thick, dry coal seam, and an explosive dust, there have been at least three instances of gas explosions extending up to 1000 ft. or more and blowing

out concrete overcasts or stoppings, yet dying out on reaching wet or recently sprinkled zones. In a violent explosion in a Western unsprinkled coal mine, the explosion died on reaching two entries with about 500 ft. of decidedly wet sides, top, and floor; in another violent explosion in a Western unwatered mine, every man in the mine was killed and the mine was wrecked, but the explosion stopped almost dead at a wet region. In Utah, while there were two bad explosions in 1924, there have been numerous instances at least one of them in 1924, where gas ignitions accompanied by considerable heat and force have been stopped by well watered workings; in fact, there are few operators of any considerable number of years of experience in Utah coal mines who cannot cite several instances in which widespread extensions of incipient explosions have undoubtedly been stopped by water; hence Utah's loyalty to watering methods.

In Pennsylvania, the writer aided in the investigation of an explosion that killed every man within a dry panel; but fortunately the flame did not get out of the panel because the four openings to the panel were wet (top, sides, and floor). In this instance, while nearly 20 were killed within the panel, the mine had over 500 other workers and in general the workings were dry and dusty; here the naturally wet condition of some fortunately located workings undoubtedly saved several hundred lives. In an Alabama gas explosion, every man in the immediate neighborhood was killed; but in proceeding outwards, the explosion encountered wet or sprinkled territory and died out. This list of explosions stopped by water can be readily extended, as the writer has records of at least twenty authentic cases. As previously stated, while there have been explosions in mines having sprinkling systems, the trouble almost invariably has not been with the system but with violations of the system, and rock-dusting in mines will also fail if rock-dusting is neglected. Those people who figure on long-time immunity from danger when rock-dusting has been done once will be greatly disappointed, for rock-dusting can become ineffective under certain conditions within a few days, even within a few hours, after having been placed. Mines that regard rock-dusting as a panacea permitting relaxation or abandonment of other precautionary measures are likely to learn that rock-dusting has decided limitations while having also much merit if done with judgment.

Conclusion

Both sprinkling and rock-dusting should be done in every coal mine—the sprinkling largely at or around the face; the rock-dusting in the entries (particularly those on intake air), and both methods should cover ribs, roof, floor, and timbers. Both methods must be kept in condition, and to do this constant and continuous supervision must be

exercised and much rock-dusting as well as sprinkling work must be done continually. If efficient sprinkling is not done at the face, not only will ignitions be made easier and more frequent but also the coal from dry "bug dust," blasting, shoveling, etc. at the face and from the top of loaded cars and the bottom of empty cars, as well as from coal spilled on roadways, will, within a very short time, cause rock-dusted ribs, floors, roof, and timbers of entries, abandoned workings, etc. to be so covered with fine dry dust as to be easily available for feeding flame and propagating an explosion. How easily this may be done can readily be figured when it is considered that 25 per cent. the very fine dry coal dust that settles out of the air mixed with 75 per cent. of rock dust will readily propagate an explosion in some of our Western mines; probably, in some cases 20 per cent. or less of very fine dry coal dust will propagate an explosion. Some mines that blast after the working shift have sufficient fine dry dust deposited from the air after the blast and covering ribs, roof, timbers, etc. near the face so that if rock-dusted daily the face region surfaces would have an inflammable dust covering when the shift went to work.

It seems to the writer that rock-dusting in coal mines without simultaneous use of watering methods at the face is analogous to such abominable practices as adoption of electric safety lamps and allowing smoking at the faces, or forcing use of electric safety lamps, and blasting with fuse and black powder with the shift in the mine, or spending money on electric safety lamps and then saving the money by slowing down the fan or reducing the amount expended on overcasts, stoppings, or brattice cloth. Whether sprinkling is used or rock-dusting is put into operation, or even if both are used, constant attention must be given and renewals not stinted; also such adjuncts as keeping up ventilation, restriction or prohibition of open lights or of any kind of flame underground, sealing of abandoned territory, using nothing but permissible explosives in permissible quantities in blasting, prohibition of blasting with the working shift in the mine, and other good up-to-date mining practices should be extended rather than relaxed or abandoned.

In connection with rock-dusting of coal mines, while much attention and much money are being expended at the present time, it is curious how little the mining men of the United States use the wealth of information on rock-dusting prepared for them by the Bureau of Mines, especially the data in *Bulletins* 20 and 167 and in *Technical Paper* No. 84. These publications should be carefully studied by up-to-date coal-mine safety and operating men of the United States; *Bulletin* 167 particularly should be at their finger tips.

As to the kind of rock dust to be used, in so far as health is concerned; after having spent at least seven years in studying the effect of dusts on health, in both coal and metal mines, the writer believes that if water

is used at the working faces and rock dust is restricted to the entries and non-working territory, the silica content of dust can be ignored and the writer would not hesitate to recommend the use of dust for rock-dusting and for rock-dust barriers, with silica content 90 per cent. or over provided the dust had less than 10 per cent. combustible and was sufficiently fine. Dust is dangerous to health only if in the air around workers in such manner that the workers breathe large quantities of very finely divided dust into the lungs. By experiment it has been found that except at dry, poorly ventilated working faces, the air in rock-dusted mines has so little rock dust in suspension as to be negligible. But, if rock-dusting is done up to and at dry working faces, and no water is used, there is no doubt that the number of lives saved by the rock-dusting in preventing explosion will be far more than counterbalanced by lives lost due to respiratory diseases such as miner's consumption, bronchitis, miner's asthma, etc., caused by breathing dust. The real answer to the problem of prevention of coal-mine explosions is that neither watering nor rock-dusting should be relied on alone, but that sane, safe reasoning demands that both be used and both be kept under careful supervision and maintained even more carefully than is ventilation.

DISCUSSION

George S. Rice, Washington, D. C. (written discussion).—The author has forcefully presented the merits of humidifying in bituminous coal mines, and has emphasized the fact that, to be effective, humidifying must be systematically done. He tells how humidifying is carried on in certain mines in New Mexico, Colorado, and Utah; but I question whether the employees can be relied on in all mines, day in and day out, to exercise the degree of carefulness he describes. Humidifying in the Rocky Mountain mines is not new. An explosion disaster at the Dawson mine, New Mexico, in 1913, in which 263 men were killed, was attributed by the State Inspector to the omission of watering over a holiday, which shows that in that mine watering was supposed to be done every day.

Utah has required the use of hose at every face for the past 25 years and sprays have been used, yet disastrous explosions have occurred in that state. The new mining regulations, by requiring the use of water sprays on all mining machines, have added to the safety measures, but mining machines have been extensively used in Utah only in recent years; in 1912, only 4 per cent. of the total output was machine mined. In any case, this wetting has to do with lessening the formation of coal dust and ignition at the face; it does not prevent direct ignition of coal dust back from the face or prevent the propagation by coal dust of an explosion started by the ignition of a body of firedamp at the face.

Propagation must be prevented by intensive continuous watering, such as he describes, or by efficient rock-dusting. I favor generalized rock-dusting back from the face[1] and think that the burden of proof that watering is better rests on those who favor it, for explosion disasters have been occuring not only in this country but in Great Britain and quite recently in Germany in mines where watering has been done, or in mines considered naturally wet.

This paper seems to indicate that the usefulness of rock-dusting is limited to the outer part of an intake haulage road, where freezing of water may occur in cold weather, for use in barriers, and in assisting in the process of wetting coal dust; the latter feature is described in an earlier paper.[2]

Undoubtedly, the path of explosions in mines has often been limited by wet places; but on the other hand, explosions have traversed long stretches where water has lain over the rails. Each such case must be considered separately, as it depends on whether large amounts of coal dust, on which the explosion feeds, are carried by the advance air waves from places farther back, or whether less coal dust was carried and when that was consumed there was no coal dust in the wet zone to bring into suspension, so that branch of the explosion would cease. In the case of the Palos, Ala., explosion (in 1910) there was a wet, untimbered incline about ¼ mile long, through rock, with no evidence of coal dust on the walls, yet a sheet of flame extended about 200 ft. from the mouth of the mine and burned to death a postman on a bridge; also, there were thick clots of coke on a railroad trestle that crossed over the mouth of the mine.

The author suggests that in the spring, summer, and fall the coal dust in Eastern coal mines tends to be made inert by the warm, moist, intaking air; past records do not bear this out. Eavenson shows[3] that in this country (from 1839 to 1912) more explosions occurred in January than in any other month, but that explosions occurred in every month and that there were over one-half as many in August, the minimum month, as in January. As bituminous coal mines usually work only part time in the summer, there is less time of exposure to explosions. It is freely admitted that in new mines, or mines of small area, the effect of warm intaking air is of material benefit; but in extensive mines, the amount of moistening of coal dust in the interior through this natural agency has little effect in preventing explosions, as shown by Mr. Eavenson's statistics.

The author indicates that greater natural dangers are encountered in Rocky Mountain coal mines than in Eastern coal mines, but, while

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[1] Review of Coal-dust Investigations. See p. 1130, this volume.

[2] George S. Rice: Investigations of Coal Dust Explosions. *Trans.* (1914) **50**, 567.

[3] H. N. Eavenson: Coal Mine Explosions Caused by Gas or Dust. *Trans.* (1914) **50**, 588; also Table 2, 605.

dangers should not be belittled, certainly, many Eastern mines have serious gas and coal-dust problems. Some readers may conclude, from the author's statements, that the coal dust in the Rocky Mountain mines is so much more dangerous than that of Eastern mines as to be difficult to neutralize by rock-dusting. The Bureau of Mines laboratory experiments giving relative pressures for different dusts, cited by the author, were empiric. It was early determined by the Bureau's coal-dust investigators that pressures were not indicative of relative explosibility, which conclusion is now accepted by the British scientists. Moreover, to make the laboratory tests, the coal had to be ground so that all of it would pass through 200 mesh, which destroyed the natural structures of the particles as found in average samples of mine dusts. When the laboratory tests quoted were found to obtain very different results from practical large-scale testing, it was decided, ten years ago, to drop that method of experimenting.

The author quotes from Bureau of Mines *Bulletin* 167 (p. 344) that a southern Colorado coal dust requires 82 per cent. incombustible to prevent propagation, in contrast to 77 per cent. for Pittsburgh coal dust; this was for pulverized dust 75 to 85 per cent. through 200 mesh, which is finer than any considerable amount of dust averages from any mine. The practical comparison is on the basis of dust of which 20 per cent. passes through 200 mesh—an average size proportion found in mines. With this size, the Colorado dust has the same limiting mixture as Pittsburgh dust, 64 per cent. incombustible (ash of coal plus shale, or dirt, plus moisture).

Recent (unpublished) tests at the Experimental Mine have shown that Utah coal dusts of similar size (20 per cent. through 200 mesh) have no higher explosibility than Pittsburgh coal dust. The resin content mentioned by the author, although highly explosive when picked out and tried by itself, forms so little of the total weight of coal that it has no appreciable effect on the explosibility of the coal dust as a whole.

I question the conclusion that, in the Dawson No. 1 explosion of 1923, the dust where the explosion originated had an incombustible content of 65 per cent., unless sufficient samples had been gathered at that point shortly before the explosion. It would be impossible to judge of the composition of the dust existing *prior to* the explosion from any samples gathered *after* the explosion, as the entire dust conditions of an entry in the zone of an explosion are changed by the violent gas and air movements. Tests on the Dawson coal dust (20 per cent. through 200 mesh) at the Experimental Mine indicated that 66 per cent. incombustible would prevent propagation, as compared with the 64 per cent. limit for Pittsburgh dust. "Ignition" limit would be less (probably 10 per cent. or

more), but this was not determined, as sufficient dust material for such tests was not furnished.

Apart from the question of the character of the dust on timbers, at the supposed point of origin of the explosion, I understood that it was supposed ignition resulted from the derailment of a trip of loaded cars, one containing bug dust; these cars knocked out timbers, which brought down the trolley wire and caused arcing where the wire touched the steel cars. Such derailment would stir up a large amount of fine, pure coal dust, which would likely be ignited by the arcing and give an initiatory explosion.

The author compares this with an ignition test of the same size dust, using 8 per cent. water in addition to natural water of coal (2.8 per cent.). Ignition was not obtained, but the flame traveled 175 ft. from the 4-lb. black-powder shot. If a stronger shot had been fired or only 1 per cent. of firedamp were present, 8 per cent. added water would not be nearly enough to prevent "ignition" and still more water would be required to prevent "propagation." Tests with Pittsburgh dust of 20 per cent., through 200 mesh, required over 16 per cent. water, and for pulverized dust, 30 per cent. water to prevent propagation. The author is skeptical as to 30 per cent. being necessary, based on his observations of wetted "bug dust" from machine mining. But "bug dust" is relatively coarse; screen tests have indicated that usually less than 20 per cent. will pass through 200 mesh. In pulverizing, the aggregate surface of the coal-dust particles increases nearly as the cube of the diameters, which causes a great increase in the ability to hold water by a mass of dust. This explains the apparent discrepancy in the amount of water required for different sizes of coal dust to wet it so that it will not be dislodged and brought into the air by violent air currents.[4]

Dry rock dust, on the other hand, does not depend on preventing the coal dust from getting into the air; it is raised by the same concussion that raises the coal dust and extinguishes by absorption of heat and mechanical interposition of inert particles.

The author suggests that rock-dusting requires about four times as much rock dust as coal dust to prevent propagation. That may or may not call for a large amount of rock-dusting, depending on the care in preventing the making of coal dust. However, four times gives a very large margin of safety as the recommendations of the Bureau of Mines engineers for a number of Rocky Mountain coal-mine dusts (20 per cent. through 200 mesh) varied from 64 to 69 per cent. incombustible to prevent "propagation;" that is, continuance of an initiatory explosion of gas or pure coal dust. The coals tested carried from 10 to 16 per cent.

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[4] George S. Rice, L M. Jones, W L. Egy, and H. P. Greenwald: Coal-dust Explosion Tests in the Experimental Mine. 1913 to 1918, Inclusive Bur. of Mines *Bull.* 167 (1922) 399, Fig. 48.

incombustible, ash plus moisture. Taking the higher limit, 69 per cent., and the least incombustible in the coal, 10 per cent., there would be in the mixture 34.4 per cent. coal and 65.6 per cent. limestone or shale dust. This is less than twice as much rock dust as coal dust but it prevented propagation.

In his conclusions, the author concedes that there is need of both rock-dusting and watering efficiently done. He also implies that rock-dust barriers may be advantageous, but does not comment on them in detail. From previous correspondence with him I think that he is apprehensive, as am I, that the designs of some of the barriers that have been installed disregard certain fundamental factors that Bureau of Mines investigators have studied and reported on in the Experimental Mine testing; and many barriers observed in mines are underloaded. Experience in testing has shown that the loading should be about 100 lb. of rock dust per square foot of cross-section of entry way.

As a whole, I believe that the author's views and mine are not so far apart as the wording indicates. His paper is admirable in bringing strongly to the attention of bituminous-coal-mining men the need of increased effort to prevent appalling explosion disasters. I take this occasion, now that Mr. Harrington is no longer in the Bureau of Mines service, based on ten years of close association with him, to express my admiration for his untiring, courageous, and splendid leadership in the cause of safety in mining.

D. Harrington (author's reply to discussion).—It is difficult to rely on mine employees, or even mine management, to exercise the degree of carefulness necessary in watering methods to hold mines safe; this statement is applicable to rock-dusting in almost the same degree as to sprinkling; in fact, if rock-dusting is to be used at and around the face regions, in my opinion sprinkling methods will be much more fool- or carelessness-proof than will rock-dusting.

Mr. Rice is in error as to the use of water in the mines at Dawson, N. M., before the explosion in 1913; watering was being done very ineffectively and intermittently, as shown by the fact that after the 1913 explosion several carloads of water pipe were placed in the mines. Mr. Rice is also misinformed as to "use of hose at every face for the past 25 years" in Utah coal mines; it is true that water lines were called for but there was no requirement as to hose until the regulation went into effect in September, 1920. Even then, use of hose at the face was optional, as evidenced by the words: "such hose shall be provided by the operator for each and every miner *who may request therefor.*" As a matter of fact, comparatively few faces were provided with hose until the new Utah regulations made use of hose at the face obligatory.

While use of water on the cutter-bar of mining machines certainly will not "prevent direct ignition of coal dust back from the face or

prevent propagation by coal dust of an explosion started by the ignition of a body of firedamp at the face," it certainly will reduce the amount of coal dust likely to be found either at the face or back from the face. The Pittsburgh Coal Co. recognizes this, as General Manager Neale, in a paper on rock-dusting at Cincinnati, in May, 1925, recognized the very definite advantage of use of water on the cutter-bar; many coal companies in eastern and southern states also are using this system.

Notwithstanding the Eavenson statistics, with which I am not familiar, there is absolutely no doubt of the fact that many eastern mines do have extensive sweating during various parts of the year, during which period mine workings are decidedly wet. This wetting is so bad, due to sweating, in the Experimental Mine of the Bureau of Mines near Pittsburgh, that explosion tests by the Bureau must be suspended during the sweating months; moreover, the fact that explosions occur during the slack working periods in spring and summer, as reported by Mr. Rice, is due usually to relaxation in precautionary measures to aid in decreasing cost; and to poor ventilation, shooting, and other methods, rather than to any other cause.

I disagree decidedly with Mr. Rice's conclusion that the Bureau of Mines laboratory experiments on coal explosibility are unreliable or merely of empiric nature; certainly the statement that pressures obtained in laboratory experimental work are not indicative of relative explosibility is not the opinion of at least two men who were engaged in that experimental work and with whom I have talked personally. Nor do I agree that the resin content of coal, because of its relatively small amount compared to total weight of coal, is of "no appreciable effect on explosibility of the coal dust as a whole." The resin is present chiefly in thin layers, very brittle and quickly reduced to dust, and is exposed on very many face clats, and the very fine settled dust on ribs, roof, and timbers (the most dangerous kind of dust in a mine) has a high resin content in many Utah mines. Recently, I took some settled coal dust upon a rock-dusted rib, in a Utah mine, with resinous coal. An analysis showed 70 per cent. ash, yet when the dry dust was sifted over a lighted match, it flamed, thus indicating the high degree of inflammability of Utah coal dust, plus resin, even when 70 per cent. of rock dust was present. Mr. Rice will admit that if finely divided black powder were distributed over coal surfaces, there would be appreciable effect upon explosibility even if only relatively small amounts of black powder were used. The fine dry friable resin in Utah's coal seams is but a little less inflammable than black powder. The recent Bureau of Mines' tests of Utah coals, to which Mr. Rice refers, ignore this matter of resin, hence get low explosibility results; but unfortunately Utah coal mines in actual operation are unable to ignore or to eliminate the resin, and if they are to avoid disaster, they must take measures toward checking its menacing influence.

As to Mr. Rice's skepticism that an extremely fine dust with 65 per cent. inert matter, settled upon timbers, would ignite, to start the Dawson explosion, after having been subjected to the intense heat of an electric arc, it has been recently demonstrated that a Utah rib dust, with 70 per cent. inert matter, ignited when sifted over the flame of ordinary lighted match.

Mr. Rice says that the necessary percentage of rock dust depends "on the care in preventing the making of coal dust," yet throughout his discussion of this paper he seems to take a definite stand against the use of water to prevent formation of dust. In my opinion, this is exactly where the rock-dust enthusiasts fall down, as rock-dusting does not, in any manner, aid in prevention of dust formation, or its dissemination—in fact, rock-dusting intensifies mine dustiness.

Mr. Rice is in error when he states that the paper in question "seems to indicate that the usefulness of rock-dusting is limited to the outer part of an intake haulage road, where freezing of water may occur in cold weather, for use in barriers and in assisting in the process of wetting coal dust." The first part of the conclusions in the paper states definitely that "both sprinkling and rock-dusting should be done in every coal mine—the sprinkling largely at or around the face; the rock-dusting at the entries (particularly those on intake air)."

In fact, the above sentiment is found throughout the paper and the thought throughout is that face sprinkling will be almost indispensable if rock-dusting of other parts of the mine is to be successful. I am confident that Mr. Rice himself is in favor of the use of water at and around the face; in any event, he is on record in some of his publications to that effect.

Mr. Rice's written discussion of the paper in question reaches me when I am sadly pressed for time, hence it is not feasible to answer all of his arguments. I agree that his ideas and mine are in the aggregate essentially similar, but with the difference that Mr. Rice seems, in this discussion, to wish to burn his bridges behind him, in so far as refers to his past advocacy of use of water, while my attitude is that watering methods should be used where experience and common sense teaches that rock-dusting as well as general mine safety and health will be aided.

Safeguarding Coal-mining Operations against Danger from Oil and Gas Wells

By A. W. Hesse,* Nemacolin, Pa.

(New York Meeting, February, 1925)

Twelve years ago, some coal-mine operators, mining engineers, oil and gas operators, Bureau of Mines engineers, geologists and state mine inspectors met in Pittsburgh, Pa. to discuss and solve if possible, the problems in connection with the drilling of oil and gas wells through or near coal mines and through the future coal reserves. Regulations were drafted and presented by O. P. Hood and A. G. Heggem of the Bureau of Mines.[1] There was considerable discussion of the various articles, practically all of which appear in *Bulletin* 65, but the interest aroused at that meeting was short lived. Practically none of the important coal-producing states gave the matter the consideration it should have received.

Notwithstanding the marked progress in safety work, coal mines still have an unenviable reputation for mine explosions. Our mining laws have become stricter and the enforcement, especially in Pennsylvania, more rigid, but what good will come from a rigid enforcement of the mining laws if some source of danger exists all around the mines, over which the operators have no control? It is hardly necessary to recite all the cases of natural-gas explosions published in *Bulletin* 65, but with some of them I am especially familiar. In 1912, while visiting the Miners' Hospital, at Fairmont, W. Va., my attention was called to a patient swathed in in bandages so that no part of his face and hands were visible. He had not been told that his two sons, mere boys, had died of the burns they had received in the same accident—explosion due to natural gas leaking into a country mine at Peora, Harrison Co., W. Va.

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* Chief Mining Engineer, The Buckeye Coal Co.

[1] G. S. Rice, O. P. Hood *et al.* Oil and Gas Wells through Workable Coal Beds, Bur. of Mines *Bull.* 65.

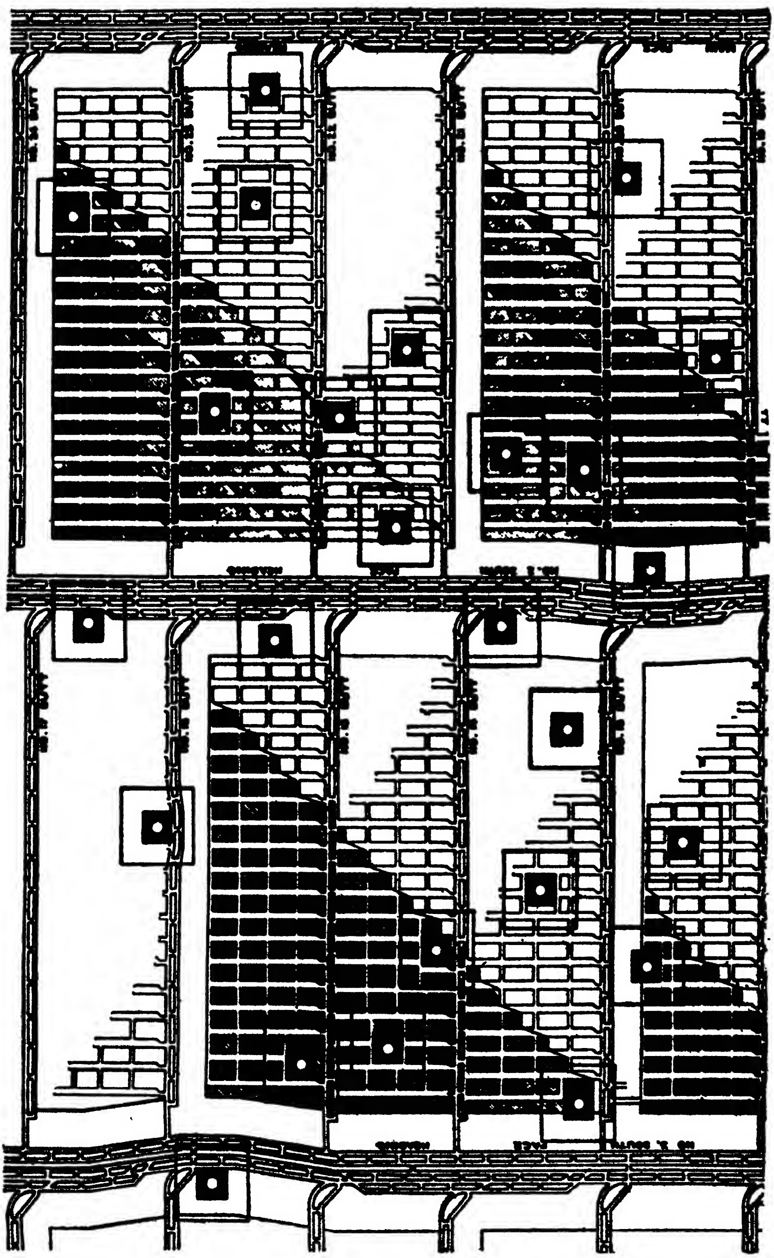

Fig. 1.—Projected plan of mine workings with gas wells surrounded by pillars of coal.

The explosion that wrecked mines 47 and 49 of the Consolidation Coal Co., at Middleton and Enterprise, W. Va., respectively, was due to gas from a well that was considered properly cemented; that is, the 8¼-in. (No. 1) casing was run in to a point 82 ft. below the Pittsburgh coal and the space between the casing and the walls of the 13-in. hole was supposedly filled with a cement mortar (1 part cement to 2 parts sand) to a point about 20 ft. above the coal. The mixture was poured in around the pipe at the top of the hole; whether or not it reached the bottom is a question. The escaping gas evidently came from the bottom of the 8¼-in. casing, as this casing was capped at the top to catch all the gas from the interior casing and tubing. Whether the gas followed the walls of the hole part way up and then spread, or spread out at the bottom and seeped up through the 82 ft. of rock strata, is mere conjecture; it did spread somewhere before it reached the coal bed, and the mine air was soon charged with natural gas coming from the floor of the mine at various places in the neighborhood of the well. That the explosion was not more disastrous was due entirely to the Consolidation Coal Company's policy of keeping all coal dust watered down in all its mines.

The explosion at Reynoldsville, W. Va., near Clarksburg, was caused, presumably, by a closed line forcing the gas down through the bottom of the outside casing, thence to the face of the single mine-entry working 1500 ft. distant. After the explosion, a 2-in. hole was drilled into the face of the entry at one point where the gas was escaping and a 1-in. pipe was inserted. The pressure of the flowing gas through this pipe showed 0.2 in. water gage, indicative of a flow of 17,560 cu. ft. per 24 hr., or 12.2 cu. ft. per minute. As the low explosive limit of methane (CH_4) is 5.5 per cent. and of ethane (C_2H_6) 4.98 per cent,[3] about 200 cu. ft. of air was necessary, with a spark or light present, to set off a minute's flow of this particular leak. This alone was sufficient to create a tremendous disturbance and, in a single entry with no provision for taking a flow of air to and away from the face, the standing air was highly charged coincident with the miner's shot. In both gaseous and non-gaseous mines, thousands of entries have standing air in them after they pass the crosscut through which the air traverses to the parallel entry, and any unexpected flow of gas quickly changes this standing air until it is like so much powder in a cannon.

In the Cañon City district of Colorado, mines have struck oil which has continued to flow for several months. Among these are the Rockvale and Coal Creek mines of the Colorado Fuel & Iron Co., adjacent to what is known as the Fremont oil field. One flow of oil, struck in the Coal Creek mine, in 1922, produced 25 bbl. per week, and was the cause of

[3] G. A. Burrell: Notes on Mine Gas Problems. *Proc.* West Virginia Coal Min. Inst. (1912) 294.

a disastrous mine fire. This flow of oil from a well would hardly be classed as a bonanza by an oil operator, but in a coal mine it is a terrible menace.

Correlation of Coal with Oil and Gas

A coincidence exists between volatile matter in coal and oil and gas accumulation;[3] coals of over 40 per cent. volatile matter have been correlated with the principal fields of oil and gas of the world. It is natural to expect that the higher volatile coals will be worked in the future, as the coals of higher fixed-carbon content become exhausted; therefore, we are just approaching this additional hazard in coal mining. Just how many wells have been drilled in these fields is uncertain, as a great many have never been surveyed and charted. Whether or not those still in service are properly cased and packed cannot be proved and those plugged may or may not have been plugged according to the laws governing that work. In the western part of Greene County, Pa., the coal is really just coming into prominence and in certain sections of that field, the drilling has been very active for a number of years. The same conditions apply in the Cameron, Littleton and other districts of West Virginia, where the coal has been given little attention until recently. In the eastern part of Greene County, Pa., two wells were drilled whose locations are not known exactly, even by the drilling company.

Once the strata are punctured and the gas or oil tapped, as long as there are casings in the hole, the well is a menace to the workings in that vicinity and to the lives of the men laboring underground. In the cases of gas leakage cited in this paper, the gas came from a capped well or from a well with the valves closed.

In 1911, the New Staunton Coal Co. sank a well near its top works, at Staunton, Ill., to ascertain whether or not there was a coal seam under the seam being worked, which was 280 ft. under the surface. When the hole reached a depth of 533 ft., a gas pocket of considerable volume was encountered, which burned for six weeks and gained widespread publicity. As a precautionary measure, the coal company left the casing in place and, in addition, walled up the pillar through which the well passed.

In 1916, a mining engineer connected with the Vinn Oil & Gas Co. asked the coal company for permission to drill for oil and gas through some coal rights purchased from a family named Schuette. At that time, the mine workings were well within the Schuette tract and the coal company refused to grant a location there or elsewhere. The oil and gas

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[3] Dividing the State of Pennsylvania into Areas Having Coal of Equal Volatile Content. *Coal Age* (Sept. 18, 1924).

company served notice on the coal company that it intended to enter and drill the Schuette tract, whereupon the coal company filed an injunction against the oil and gas company in the Circuit Court of Madison County, October Term, 1916. The Court ruled that the oil and gas company could not drill through the Schuette tract because the workings had reached that point, but gave it the right to drill through coal owned by the coal company beyond the workings. The coal company was forced to indicate a location and the well was drilled. The territory proved dry and the matter was dropped, but two years later, the same engineer, representing the Johnson Oil & Gas Co., asked the New Staunton Coal Co. for a location comparatively close to the main and ventilating shafts, because the gas pocket was tapped near that point in 1911. The coal company refused to give a location at any point in its coal field, and nothing further developed.

Court proceedings are not desirable methods for establishing the status of the two industries, but with coal mines spreading into gas and oil fields not heretofore exploited, with the accompanying danger of striking wells and gas or oil feeders from the leakage of worn-out packers and casings or abandoned holes, there must necessarily follow a common understanding as to the protection of both interests.

Policies of the Past

In 1908, Dr. I. C. White, state geologist of West Virginia, before the American Mining Congress, called attention to the situation as "an ever-impending peril to deep mining over oil and gas areas, and to unknown waste of coal and precious lives that may possibly result therefrom." The Consolidation Coal Co. in West Virginia was not long in recognizing this possibility and that same year began to take an active interest in the drilling of wells through its coal in the Fairmont field. The oil and gas companies were asked to make provision in their drilling operations to prevent the possible escape of oil or gas from the casings into the coal or mines.

As a result of these requests, one company drilled a 15-in. hole to a depth of about 30 ft. below the bottom of the coal, ran in a 10-in. casing, then poured grout, made up of one part cement and two parts sand, around the casing from the bottom up to a point about 30 ft. above the top of the coal. The grout was poured through a 2-in. pipe, which was run from the top to the bottom of the hole on the outside of the casing; as the hole filled up, the pipe was raised a joint at a time. This method assured the placing of the grout on the bottom, at least.

Another company drilled a 13-in. hole to the depth mentioned and used either a 10 or 8¼-in. casing, but adopted another method of placing the grout. Before the last joint of the casing was put on, the entire mixture of grout was poured into the hole, thus filling the entire area

of the 13-in. hole. Then the casing was dropped onto the bottom and the grout on the interior of the casing was bailed out and poured in around it at the top. Other companies poured the grout around the casing at the top.

Some companies could not see the value of any of these plans and cemented their wells only after considerable pressure was brought to bear on them; but in practically every case the cementing was done as soon as the hole reached the depths mentioned. This practice, I am told, is still being carried out in the Fairmont field. In Greene County, Pa., the first and third plans are used in cementing the first casing; but companies want to postpone (and in a number of cases have postponed) the cementing until they find out how much the wells are worth. By the time a well is proved, the probability is that the hole has caved or bridged so that there is little likelihood of the grout ever reaching the bottom of the hole; as evidence of this, in some instances, the grout ran out over the top long before the required number of batches were run in.

Plugging and Abandoning Wells

The plugging and abandoning of wells have been covered in nearly every state by law, and the oil and gas companies have thus been held to some semblance of protecting the coal operator; but some of these laws need revision. For instance, Section I of the Pennsylvania General Assembly, Act of 1921. ". . . . In abandoning any well which has been drilled through marketable coal, after the inside casing has been drawn, there shall be placed a two (2) inch vent pipe extending from a point thirty (30) feet below the coal bed for a distance of eighty (80) feet in height; said pipe to be encased in cement, after which the outside casing may be removed." With a pipe extending only, say, 44 ft. above the coal seam, and a cover of 600 or 700 ft. of rock and soil sediment, an accumulation of gas could easily gain access to the coal seam. Section II of this same Act states "Whenever the production of any gas well is not sufficient, in the estimation of the owner, to justify leaving the casing or casings in the well, the well may be utilized through tubing placed on a packer, and, after cement and sand has been poured on the packer to a depth of not less than ten (10) feet, the casing or casings may be pulled and the hole outside of the tubing filled with sand, cement, rock, sediment, clay or other material, to a point at least thirty (30) feet above the highest producing sand, so as to completely shut off all the *water** from the various sands, after which the casing may be drawn. Upon the abandonment of such gas well, if the plug or bridge shall be placed in the tubing at a point near the depth at which the packer was set, and cement

* Editor's italics.

and sand poured in on said plug or bridge to a depth of not less than thirty (30) feet, it shall be held a compliance with the provisions of this act relating to plugging and abandoning of wells." Without any intention of reflecting upon the sincerity of the oil and gas operators in their plugging operations, it may be considered doubtful if many will use sand or cement when "clay or other material" is permissible. Also, what well is abandoned until the production of gas is insufficient to justify leaving the casings in the well? It leaves the matter entirely to the judgment of the owner and it is not a matter of plugging the well to prevent the escape of gas, but to shut off the water from the various sands. It is the poorest law ever passed for the protection of coal operations and the safety of human life; especially poor compared with the intelligent draft of proposed regulations submitted by the Bureau of Mines at the Pittsburgh meeting in 1913.

Action in Various States

The State of Ohio has gone into drilling, mapping and plugging of wells quite carefully.[4] Illinois also has given the matter of oil and gas wells some consideration for the protection of the coal interests. Indiana has some good regulations affecting oil and gas development, and the plugging of wells; but none directly governing the relationship of the coal and the oil and gas industries. However, "The (Indiana) commission may make rules and regulations authorized by this act and such others as may be necessary in their judgment to carry out its provisions, and such rules and regulations, when approved by the governor, and promulgated as hereinafter provided, shall have the force and effect of law. . . ." Tennessee has not yet had a conflict of these interests, although Fentress County is now producing both coal and oil and oil pools are sometimes discovered in unexpected places. No legislation has been passed and none is likely to be until the wells begin to penetrate the seams under development. The Railroad Commission of Texas governs the drilling, casing, etc. of gas and oil wells in that state, and H. E. Bell, chief supervisor of the Oil and Gas Division, writes, "Inasmuch as we have had no gas or oil development around or near the coal fields of the state, this question has never presented itself to us for solution." West Virginia has a regulation covering the plugging of oil and gas wells; but when that is said, all is said. Colorado in its laws relating to the Inspection of Oils and Paints, Sec. 30, provides for the plugging of abandoned wells by requiring wood plugs to be placed below and above the water-bearing formations; Sec. 32 allows the drilling of wells as near as 15 ft. from the mine haulage or airway; Sec. 33 provides for preventing surface water from entering the mine by means of the casing; Sec. 34 requires that when oil or gas is

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[4] *Bull.* Indust. Com. of Ohio, 4, No. 7.

found and the well passes through the coal seam or mine workings, they shall be sufficiently protected by casing so that the gas or oil shall not come in contact with the coal seams or enter the excavation of worked out seams. The state coal mine inspector is notified after a well drills through a coal seam or penetrates somebody's coal mine, by the state oil inspector, who first gets the information from the owner of the well.

Coöperation between Operators

Wherever oil and gas wells have been drilled through seams of coal under development, the coal operator has tried to protect his mine and employees by seeking the coöperation of the oil and gas operator and by leaving a certain quantity of his coal in the ground, around each well. In the Fairmont field, the Consolidation Coal Co. lays off a block of coal 100 ft. square up to a 200-ft. cover. With an increase of cover, the block is increased on a ratio of one-half to one, until the cover reaches 400 ft., at which point the block is 200 ft. square. For covering greater than 400 ft., the size of the block of coal is the same. Frank Haas says that mining has been completed around several wells in the Fairmont field, each protected by the full-size pillar, with apparently no damage to any well; at least, no leakage of gas has been discovered. The New England Fuel & Transportation Co., in the Fairmont field, deviates somewhat from this practice by leaving a circle with a radius of 100 ft. around the well. The coal mine of the Four States Coal Co., Four States, W. Va., is protected by the methods already stated, during drilling operations, and when the coal is mined around a well a block of coal 100 ft. square is provided for its protection. When a well is plugged, the coal company is usually notified and an inspector is sent to witness the plugging. Mr. Beeson, of the Four States Company, believes that in a developing field similar to the one in which his company is operating larger blocks of coal around gas or oil wells are advisable. The practice in the Pittsburgh field is to leave a block of coal only 40 ft. square around a well; also this practice seems to prevail elsewhere, although originally the amount left was usually at least 100 ft. square. This seems to be courting danger, in view of the fact that 100-ft. barriers between main entries and pillar robbing have been known to spall off under a 500-ft. cover and cause bottom heaving in the entries. Data gathered by the Committee on Ground Movement and Subsidence bear me out in the opinion that under heavy cover with the coal taken from all four sides of a 40-ft. block around a well, there is considerable danger of strata movement over this area, with the probability of breaking the casing, or breaking the hole, if there is anything left in the hole.

Essential Points to Consider

Too much has been left to the courts of equity for settlement and it appears that unless some rules are formulated, for the guidance of both parties, some serious accidents will occur to mar the efforts that are now being put forth for the welfare of our miners.

Before plugging any well from which oil or gas has been taken in any quantity, the rock pressure should be ascertained, and this should determine the method to be followed in sealing off the possible escape of gas. The well that caused the Middleton-Enterprise explosion had at least 850 lb. rock pressure, and forced the gas up through 82 ft. of rock or by the 82 ft. of cemented casing. It is hardly possible that with an accumulated pressure of several hundred pounds, a wood plug followed by 30 ft. of cement mortar with loose rock piled on top would be sufficient to contain the gas. The old wells do not have even 30 ft. of cement in them and the results are showing on the surface. There is one not far from Nemacolin, Pa., there was one not far from Barrackville, W. Va., and as a boy I frequently visited one in the outskirts of Wheeling, W. Va. No doubt there are a great many more.

The cementing of the No. 1, or outside, casing where it passes through the coal has been done, in a great many cases, in a haphazard manner. Some companies in the Greene County field of Pennsylvania have refused to cement in the No. 1 casing until the drilling was finished which, in nearly every case, meant that the cement never reached the bottom of the hole, because caves had occurred between the time the first casing was put in and the finish of the drilling. J. W. Devison, of the New England Fuel & Transportation Co., says: "In the recent past we have had some trouble with certain oil and gas companies refusing to comply with the custom of this field." He referred to the Fairmont field. Certainly coal operators do not wish to deprive the drilling companies of the enjoyment of their resources underneath the coal beds; but some oil and gas producers ignore the reciprocal duties imposed by nature and recognized by the courts. Why were coal-mining laws necessary? Because explosions and accidents made it apparent that things were not being done in the safest manner. We have had explosions and fires due to oil and gas wells. Must we wait until they occur more frequently or on a larger scale? With properly worded laws and the same standard of inspection as prevails in Pennsylvania coal mines, we will have taken at least a step in the right direction for safeguarding human life. The companies that are following the right lines, and there are several, need have no fear of such regulation. Their coöperation is appreciated, where it has been voluntary in their locations and drilling, and it will be appreciated in any proposed legislation. Judge Burton's opinion, handed down in Macoupin County, Ill., in injunction suit against drilling companies, was:

"Where there is reasonable ground to expect or believe that the drilling for oil or gas through a coal seam or mine may materially increase the hazard or the danger to the persons or lives of those engaged in the active operations of the mine beneath the surface, the enjoyment of the right of the production of oil or gas may be surrendered partially or postponed as circumstances may require. The (Illinois) General Assembly has enacted laws dealing with some of the questions. Much more is needed to be done. Especially is this true as to terms and requirements for the drilling of wells for oil and gas through the working and abandoned parts of coal mines."

The American Institute of Mining and Metallurgical Engineers can do much toward helping to decide, after a careful investigation, how oil and gas wells should be drilled, protected and plugged, and what redress the coal operator shall have for the quantity of coal rendered worthless by such drilling. With this information available, any body of legislators can furnish the remedy for the inadequate protection which now exists, by efficient laws and regulations.

DISCUSSION

A. W. HESSE.—The well under investigation, No. 101, Fig. 2, was started about Sept. 5, 1921, and drilled-in in November. The first hole was started with a 13-in. bit and reached the Pittsburgh coal at a depth of 563 ft.; at 602 ft. the 10-in. casing was run in and the well was continued with a 10-in. bit and 1400 ft. of 8-in. casing was put in. It was then continued to a depth of 1770 ft. and 6-in. casing put in; then continued to a depth of 2555 ft. where the gas was struck. As the well produced only about 100,000 cu. ft. per day, 2-in. tubing was used to conduct the gas to the surface and connected into the pipeline. On June 7 and 8, 1922, the 8-in. casing was pulled and an attempt was made to cement the 10-in. casing where it passed through the Pittsburgh coal. Thirteen batches of grout, consisting of one sack cement and two sacks sand, were poured in the hole around the 10-in. casing at the top of the hole. The reason given for not cementing the well earlier was that the roads were almost impassable at the time the well was drilled-in. The gas from this well was used until late in the fall of 1922, when it was plugged without our knowledge. In March, 1924, as our mine work approached the point at which we had to decide whether to take out all the coal, or leave a protecting block of coal around the well, we discussed the matter with the owners and learned that the well had been plugged and succeeded in obtaining an affidavit to that effect on May 22. This affidavit showed that the well was bridged at 2550 ft. and filled with rock and sand pumpings to 2382 ft. At this point a wooden plug was driven, on top of which rock and sand pumpings were filled to a depth of 2330 ft.; then the well

was bridged at 1960 ft. depth and filled with rock and sand pumpings to 1825 ft., at which point a lead plug was driven and the well filled with rock and sand pumpings to a depth of 1780 ft. All the casing had been pulled with the exception of the 10-in. of which 400 ft. had to be left in the hole.

Not being satisfied with the manner in which this well had been handled, we approached it with our mine workings as illustrated in Fig. 3. When the location of the first hole was reached, a line was set by transit and, on Nov. 30, 1924, the first hole was drilled to a depth of 17 ft.; a second, 12 in. to the right and parallel to the first to a depth of 10 ft.; a third 24 in. to the right of No. 1 and parallel thereto for a depth of

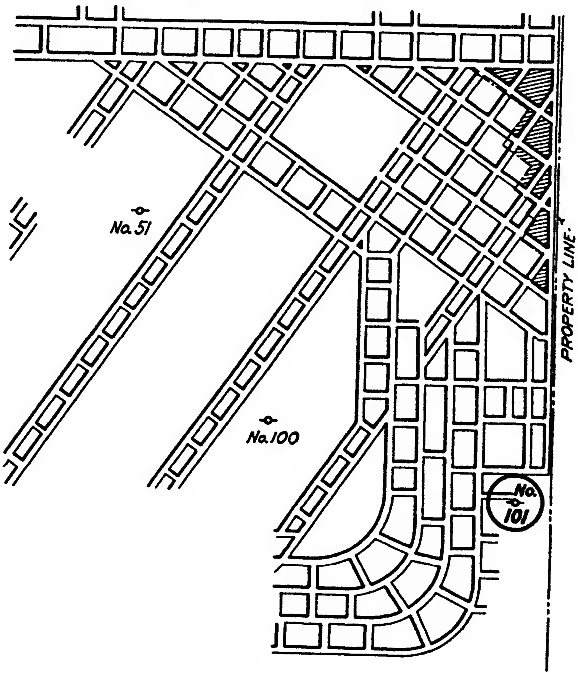

Fig. 2.—Sketch showing general location of gas well No. 101.

8 ft.; a fourth 36 in. to the right of No. 1 hole, but turned slightly to the right of the parallel line No. 1—all missed the well. A fifth hole was then drilled 15 in. to the left of No. 1, 10 ft. deep and parallel to the rib of the room and three more holes likewise drilled across the face of the room, to make sure that the well would not be struck by a coal-cutting machine when the next cut was taken out. After the next cut was taken across the face, a 3-ft. cut was taken out on the line of the cross-cut to the right. After drilling several holes into this cross-cut, one struck the casing about 13 ft. from the center line of the room. Quite a flow of water gushed forth under sufficient pressure to throw the 10-ft. augur across the room and the odor of gas and oil was so strong that it partly overcame a fireboss

standing in one corner at the face of the room. The fact that this water was released showed that the grout had not sealed off the 10-in. casing where it penetrated the coal seam, and no doubt never reached the bottom of the casing. After flowing considerable water, the hole was plugged and allowed to remain until the next day, when the augur was again poked into the hole, bringing forth another flow of water. On Dec. 5, the water was again released and apparently the hole drained out, or bridged above

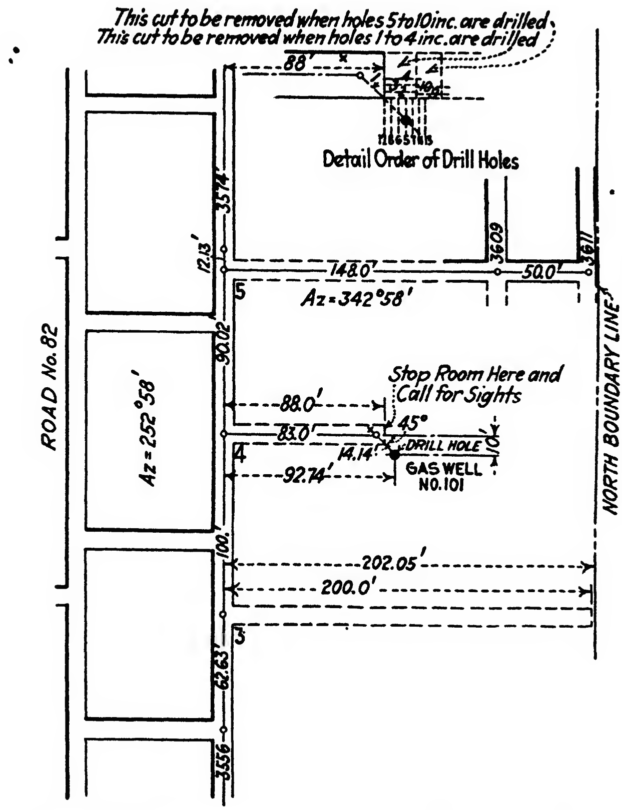

FIG. 3.—METHOD OF APPROACHING GAS WELL NO. 101.

so that it was possible to leave out the plug. It was then decided, in order to avoid any possible flow of surface water, or water from some upper strata drowning us out, to drill two more holes and grout around the 10-in. casing as far down and as far up as possible, without puncturing the casing. Preparations were immediately made and on Dec. 10, holes and pipe were placed approximately as shown in Fig. 4. The grout machine was attached to the center hole *B* and five batches of grout (each batch consisting of 1 sack cement and 1 sack sand) were forced in around

the casing; when the fifth batch was forced in, the grout vented out of the bottom hole *A*. The bottom hole *A* was then closed and the sixth batch forced clear water out of the top hole *C*. When the eighth batch was poured in, grout came from the top hole *C*, which was then plugged and the grouting was continued. After twenty-nine batches were forced in,

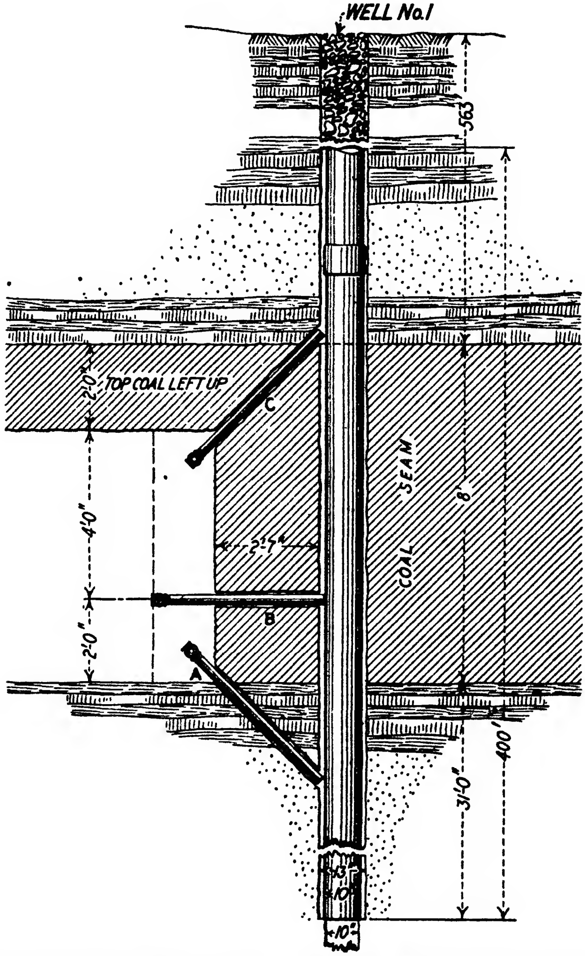

FIG. 4.—SECTION OF GAS WELL NO. 101, SHOWING METHOD OF GROUTING AROUND ABANDONED CASING.

the center hole *B* became plugged. The hose from the grout machine was then taken off, but no grout could be located in the center hole *B* back to the casing. The top hole *C* was then opened and likewise showed no grout in the pipe. The grout machine was then attached to the top hole *C*, and the center hole *B* was allowed to remain open. The first batch went through the top hole *C* with difficulty and the middle hole *B* vented

slightly. The next three batches went in without any venting at the middle hole *B*, but the fourth batch went in with some difficulty, while hole *B* vented some air. Some of the fifth batch had to be bypassed but the grout machine finally emptied itself through the hole. The top hole *C* would not take the sixth batch so it had to be wasted. The grout machine hose was again connected to the middle hole *B* and a batch sent through; air vented in a drill hole about 4 in. to the right of hole *B*. On the next batch, hole *B* was plugged with only a portion of the batch. Just before this batch was poured, the drill hole 4 in. to the right was plugged with wood, but the air that went in with the grout vented alongside of the pipe in hole *B*.

On Dec. 15, the coal was dug away from one side of the casing, exposing the grout that had been previously poured in, also that which was poured in on Dec. 10. At some places, the grout was only ¼ in. thick and little or none of the grout poured in by the owners of the well reached the bottom; the fact that we could force so much grout around the casing from the mine interior was conclusive evidence of this, because, from rough figuring, one batch of grout should fill about 1.42 cu. ft., or 4.18 ft. of vertical distance around the pipe. Five batches brought the grout up to the vent pipe or a distance of 21 ft. It is probable that the remainder of the distance of 31 ft. from the vent pipe to the bottom of the casing was caved. It then required about thirty-one more batches, before the head of grout became too great for the air pressure (about 90 lb.) used in the grout machine.

After the casing was exposed, a 5⁄32-in. hole was drilled through it and water spurted about 25 ft. from the casing, indicating, from a calculation of the trajectory, a head of 136 ft. The hole was again opened on Dec. 16, and the pipe allowed to drain about 24 hr., when a ½-in. hole was drilled in the casing, because the smaller hole plugged up; 45 min. later the casing was unwatered to that depth. The mine fan was exhausting, but instead of the air entering into the mine from the casing, as was expected, it traveled in the opposite direction. A few hours after the water had run out, the water gage on the ½-in. hole showed 0.07 in. on the reversed air. Evidently the well had bridged above and a vacuum formed when the water ran out; for the next day the air showed no movement through the ½-in. hole either way.

As the plugging record showed that the well had been filled to a depth of 1780 ft., or 1209 ft. below the coal, we desired to know the present situation, so a lead sinker, attached to a twine, was dropped through the ½-in. hole into the casing; the distance to the bottom was 92 ft., showing that the hole had caved full to that depth or had caved and bridged at this level.

A. Hurlburt,* Pittsburgh, Pa. (written discussion).—Running to the legislature to cure evils is an unsatisfactory method. There are now enough laws on the statute books of Pennsylvania. Coöperation between the coal companies and the large gas and oil producers is the only remedy that will satisfactorily take care of this situation. The paper gives little weight to the rights and necessities of the gas and oil operators. Where the latter companies have rights prior to the rights of the coal companies, it would seem only right that the coal companies should stand some of the expenses connected with protecting their mines; and unless a coöperative agreement can be worked out, there will be continued opposition by these companies. The gas and oil people are as anxious to protect life and property as are the coal people, but neither of us can escape our share of the responsibility.

The cause of much of the trouble is from wells long since abandoned, and by coöperating with the larger gas and oil companies, the coal companies can find the location of most of them, whether they belong to the large companies or not. Fig. 1 shows a condition rarely found. While I do not know exactly to what it refers, it undoubtedly was in an oilfield, and certainly in Pennsylvania and West Virginia the average run of holes drilled by gas and oil companies are very much further apart than are here shown.

A. W. Hesse.—The Philadelphia company was as largely responsible for the holes shown in Fig. 1 as any company drilling in that field. While I am not the author of this figure, I know its origin, having been connected with the Consolidation Coal Co. at the time this field was drilled. The holes are as close as shown, and the figure is an actual reproduction; the holes are principally oil wells. The holes were located so rapidly that we had to stake out the entries on the ground in order to prevent the various companies from drilling down through the projected entries and cutting them out worse than shown here.

T. G. Fear, Harmarville, Pa.—We have one property near Pittsburgh, 2100 acres of coal, through which 91 oil and gas wells pass at present and there may be more later. Having located all the headings in the mines for the next 50 years' operation, we have been able to have the gas and oil companies come to us for locations. The larger gas companies, the People's Gas and the Philadelphia company are very good about getting these locations and sticking to them. One individual oil operator asked for a location and after it was given him he relocated the hole himself. We put the location on the map, and if our engineer had not gone back to recheck we would probably have cut into that well with disastrous results.

* Vice-president, Equitable Gas Co.

A bill was to have been presented to the Pennsylvania Legislature that would force the smaller companies to do right and when abandoning a well to leave it properly protected.

We wanted to use an abandoned well, which was close to a creek, to carry water into the mine for sprinkling purposes. The well was located in the mine and cut into, and we found absolutely no grout. A quantity of water came down the outside of the casing. There was one well on the property that was not located definitely due to lack of data in the oil and gas company's office and the location was made approximately by information secured from the farmers. When the headings in the mine were driven near this well all precautions possible were taken but a considerable flow of water was encountered for four days from a crevice in the floor about 100 ft. from where the well was supposed to be. After the water drained off, there was a flow of gas for 24 hr. and that section of the mine had to be shut off from the other workings. The oil and gas wells constitute a very great danger and should be looked into more carefully in the future.

George H. Ashley, Harrisburg, Pa.—I understand that the bill mentioned has been withdrawn and that the oil men are proposing a new bill. The oil men claim that if the first bill were passed by the Legislature they would be out of business. They show that in Greene County, for instance, if they were to sink their wells in accordance with the bill, they would have to start with a 34-in. hole; as there was not oil enough there to justify that, they would have to pull out of the areas containing the deeper coals, as in Greene and Washington counties.

There are problems for both the oil and the coal men. The danger to the coal miners is so obvious as to need no discussion. The difficulties of the oil operators, however, are not so obvious. The grouting of these wells is not a simple, nor always a successful, operation. In a number of cases it has been found that the grouting was very insufficient. The People's Company had trouble laying grout at a great depth. When it tried to run the grout down a pipe, the sand and cement separated and the test showed a nice body of sand with cement higher up. It was necessary to lower the grout in a bucket and tip this over. It is very difficult to do that around a casing in a 13-in. well with a 10-in. casing; a bucket cannot be passed between them.

One of the suggestions of the gas men is that they buy a certain body of coal around each workable coal bed. But the amount of coal that would be lost in the closely drilled fields would be very large, so the problem is one to which we can give a good deal of thought.

George S. Rice, Washington, D. C.—Attention has been called to the number of wells through one mine shown in Fig. 1. At the Monongah Mines, there was but one well involved. The gas, however, traveled a

long way in an under stratum and burst through the floor of the mine along a line of weakness. Thus distance between a well and the open face of the surrounding pillar does not tell the whole story. My opinion, founded on the discussion at the Pittsburgh conference of 1913, is that a live well must have a surrounding casing vented to the surface, and an abandoned well should be completely filled from top to bottom with clay.

It is not wise, however, to have hasty legislation. Laws are difficult to frame, but as a result of that conference we thought we had the matter in such condition that committees for coöperation between the coal operators, geologists, and gas and oil men would follow up and determine the best way of handling the problem, Unfortunately, the matter was dropped, except for limited legislation in a few western states and some private agreements. At present, I do not believe that the coal operators, as a whole, know just what is the best thing to do or ask to have done by the oil and gas companies, to protect mines.

As indicated in the paper, we have the problems of the size of pillars to be left around a well. If the pillars are too small, the casing may be ruptured higher up in the strata overlying the coal mines where pillars are extracted. I am not presenting any new suggestions as to how the problem should be solved, but there should be some agreement among the operators as to what is the right procedure from their point of view before they take up the matter with the oil and gas men. The question of loss of coal reserves is serious, where the wells are close together. Is it feasible to extract all the coal, leaving no pillars, if back filling is done and the well casings and tubes arranged with slip joints, as I suggested in 1913, provided special safeguards and ventilation are used?

W. E. Fohl, Pittsburgh, Pa.—All mines penetrated by oil or gas wells are potentially gaseous mines and should be worked with closed lights, permissible explosives, permissible machinery, and all other precautions customary in such mines. For a number of years I have investigated all the mine accidents in Pennsylvania and West Virginia attributed to the presence of well drilling in the coal seam and have found none that would not have been avoided had the elementary precautions used in gaseous mines been observed. The same showing is found in all the published accounts of such accidents that have come to my attention.

The proper size of protecting pillars for wells might advantageously be made a subject of consideration by our Committee on Ground Movement and Subsidence. The pillar sizes named in the paper are unnecessarily large and I offer for consideration the pillar sizes suggested in 1910 by the late James Blick and myself. These range from 40 ft. square, with 20 ft. of cover, to 100 ft. square with 150 ft. of cover; thereafter they are increased 10 ft. on a side for each additional 50 ft. of cover so that for a cover thickness of 700 ft. there is assigned a protecting pillar 175 ft. square. Regulations for plugging and protecting wells should be more

specific and should be a part of our state mining laws with our present state inspection forces charged with their enforcement.

R. V. Norris, Wilkes-Barre, Pa.—The proper size of a pillar must depend on more than merely depth. Thickness and strength of bed are material factors. I have always failed to see why a pillar need be square.

W. E. Fohl.—I omitted to say that the pillar sizes suggested were calculated for a seam 7 ft. thick and were not intended for all seams regardless of thickness.

A. W. Hesse.—We are working in the Pittsburgh seam, which has butts and face cleavages. If you leave all coal within a radius of 100 ft. around a well, a great many difficulties will arise within that area. It is much easier for the miners to cut at right angles than to leave circular pillars.

S. A. Taylor, Pittsburgh, Pa.—Some states, notably Ohio, require that the exact location of every well be filed with the mining department. Sometimes the location is not very accurately made, but that is not nearly so difficult to do in Ohio as it is in Pennsylvania, as the section lines are all north and south and east and west and the locations are comparatively accurate.

F. B. Tough, Washington, D. C.—Just as soon as we study this question on a large scale, we find that it is absolutely impossible to lay out a set of conditions applicable in all cases. We cannot solve this question by putting a few generalities in the law and then attempting to have the states enforce them and maintain officers to live up to those regulations. The only way to solve this problem is to develop some method whereby the wells are so drilled and the mines so operated that you can take out all the coal. Leaving a pillar does not guarantee that the gas will not penetrate a considerable distance through crevices in the coal and cause loss of life and disaster.

A few years ago, it was suggested that all the coal around the well be taken out and a timber crib put in and filled with clay and then let the top come in. Does not that seem feasible? Just as soon as you get into deep mining, you cannot leave enough coal to support the roof without making the mine impossible.

It is necessary to look at this from two or three points that are quite different. A well, if it is unsuccessful, will be plugged and that territory abandoned; that problem is relatively easy. But suppose the well is profitable and is operated for 20 years? Then the operator must put a derrick over the hole and go to considerable expense to plug the hole.

When a well is drilled through a mine that is operating, the conditions are quite different from that case where coal may not be taken out during the present generation. Again, if the well passes through abandoned

workings, there is an entirely different drilling proposition. The old workings may permit the gas to travel to the workings actually in use and yet it may be impossible to send a gang of men to the point where the well strikes the mine. Therefore, the oil operator is faced with a difficult problem.

The abandonment of wells that have been operated for a considerable time comes in the same set of problems, whether they are in the abandoned workings of coal or in the present workings. If the oil man is merely asked to report the accurate location of his well, he will get off very easy. Surveying is reasonably inexpensive, so I do not think he would object to that at all. Unless the coal and oil and gas men get together and work together, you cannot hope to apply a fixed, inflexible rule in any branch of the mining game.

George H. Ashley.—The deepest coal beds in Greene County will run around 2000 and 2300 ft. The difficulty is not with the big companies. There is perfect willingness on both sides, with big companies to get together and work the thing out. The difficulty is with the small mutual companies, groups of farmers, and any one else who takes a notion to put down a well. They are irresponsible and have no permanent organization that may be sued after the drilling is over, and that is when the trouble arises. There will be no objection from the big company oil men to filing of locations of wells with the county clerk and turning over the locations to coal companies; the trouble will be with the small operator who simply sinks one well and if it does not get oil, the company divides the cash on hand and disbands.

C. W. Gibbs, Pittsburgh, Pa.—The bill that was presented to the Pennsylvania Legislature was certainly drastic, as the coal operators realized. One provision required that wherever a well was to be drilled through a seam of coal which was being operated within 10 miles of the location, the well must be 30 in. in diameter. That bill was withdrawn temporarily so that the petroleum and coal men could get together. Pending a solution of the question, the larger gas and petroleum companies agreed to permit any coal operators to have access to their plans, on which they keep a record of their wells and all others drilling in adjacent territory. They locate and keep close check on all wells in so far as possible.

George S. Rice.—It seems, from the trend of the discussion, we agree that it is undesirable to have hard and fast legislation regarding just how to handle the technical features of protecting from wells, but there should be some standardization of method. The coal operators should try to decide what the mining conditions and requirements should be, paying due attention to the question of saving all the coal that it is possible to

save, and then confer with the oil and gas men to see if a common standard cannot be obtained.

S. A. TAYLOR.—The plan of locating these wells and recording them with the state department is not to eliminate the burden on either side, but that those interested may know exactly where the wells are located. We have all noticed that in drawing pillars the break comes up at an angle off the face. Adjoining the mine that Mr. Fear is operating, we have the greatest break I have seen. With a vein of coal 7 ft. thick, with a covering of 600 ft., a little over 100 ft. from where the face of the pillar is left, the surface is broken to a width of 7 or 8 ft. Suppose that a well drilled through that pillar; no matter what you may have done the well would be broken. There is a question as to whether the leaving of pillars is the proper method after all. I doubt whether we have arrived at the proper solution of the problem and whether what everybody has been doing up to the present time is the right way to protect the wells and thereby the miners.

Messrs. Fohl and Blick figured stresses on the different heights, which was scientific, but they did not take into consideration the possibility that the break might occur in such a way that the well might still be broken, and what the result would be if this did occur. That possibility is of great importance to the coal-mining industry and especially will it be in Washington and Greene Counties of Pennsylvania, and there are going to be very serious problems in this matter in these and other fields in mining the coal.

S. W. MEALS,* Pittsburgh, Pa. (written discussion).—Fig. 1 shows wells surrounded by pillars of coal; to my knowledge the only condition of this kind to be found is near Shinnston, Harrison County, W. Va., where a prolific pool of oil was found and, as the oil and gas leases were held by various companies, an unusual amount of drilling was done. In the operation of all these oil wells, some of which produced as much as 6000 bbl. per day, and all had more or less gas, no damage was done to coal operations from the producing of oil from these wells. As the author states, several explosions occurred near Enterprise and Reynoldsville, Harrison County, W. Va., which were said to have been caused by natural gas escaping into the mines. This may be true. At that time the rock pressure of the gas in that section averaged about 900 lb. However, this condition has entirely changed. The rock pressure will not average over 200 lb., and in many of the fields it is necessary to pump the gas to atmosphere to secure sufficient gas to justify operations.

The condition is the same in Washington and Greene Counties, Pa., so that the day of greatest danger has passed. In sections of Greene

* President, Carnegie Natural Gas Co.

County, Pa., and Wetzel County, W. Va., a large number of wells have been and are still being drilled to the Pittsburgh coal for the gas that is found in that measure. Wells in these sections have produced as much as 1,000,000 cu. ft. in 24 hr. with a rock pressure varying from 80 to 120 lb. Paying gas has also been found in formations above the Pittsburgh coal. About three years ago, a core test was being drilled north of Waynesburg, Pa. The diamond drill penetrated a lime formation above the Pittsburgh coal and a flow of gas was found sufficient to raise the water out of the well to a height of 20 or 30 ft. above the surface; the pressure of gas continued to discharge the water for several weeks before the water finally drowned out the gas. I know of a number of locations where wells have been drilled and gas discovered in a formation above the Pittsburgh coal, some wells having produced as much as 500,000 cu. ft. of gas.

In some respects I believe the gas operations have been a blessing to the coal operator. If this gas was left in the coal seams and not removed by the gas operators, mining conditions would be in greater danger than they have ever been by reason of the drilling operations through coal fields. Most of the diastrous explosions in the coal fields happened in severe cold weather when the ground is frozen so the gas from the coal seams cannot find its way to the surface through the strata or crevice of rock and, thus following the course of least resistance, penetrates the mine workings.

We know that gas is escaping from the Pittsburgh coal in a number of places. I have witnessed it and people living in the section testify of this same condition existing as far back as any one can remember, years before the gas or oil operator was known in the locality. This condition is found in the heart of the Fairmont coal field near the No. 6 and 8 mine, where a disastrous explosion occurred some years ago. Coal operators should never permit fans to be stopped for any cause, even over week ends, during severe cold weather. A great many disasters could have been prevented if fans had not been shut down or had been run a sufficient time to clear all of the mine workings of gas, before the men were permitted to enter, especially in the severe cold weather.

Cementing casing through coal only needs the proper means and care to be done successfully. However, the coal operation would be as well protected if the oil or gas operator would leave two or three strings of casing in the well during its life, provided the space between the two outer strings of casing was protected and left open and free to permit gas to escape at all times.

When a well is to be abandoned and the inner strings of pipe removed, a better protection to the well and the coal can be made if a string of not less than 2-in. pipe with a guide on the bottom is run to a proper depth below the coal; cementing through the 2-in. tubing from this depth up to the bottom of the outer casing, removing the casing, a joint at a

time, and continuing to cement up through and to at least 40 ft. above the coal. Then fill the space around the 2-in. tubing solid to the top of the hole, protecting the pipe at the top with the proper appliance.

The size of the block of coal to be left around the well for its protection depends entirely on the lay and thickness of the strata above the coal. Who should settle for the block of coal left in to protect a well depends on the reservation in the conveyance or the priority of title. The best protection should be given to the men working the mine and I am sure the coal operators do not wish to place any unnecessary burden on the gas or oil operator. The larger oil and gas operators are ready and willing to work with the coal companies in doing the necessary thing to protect the coal operator. However, some unreasonable bills have been presented to the Legislature which, if enacted, would drive the small gas operator out of business. If the coal operators will present their problems to the gas associations in the various states, I am sure this question can be worked out satisfactorily to both parties.

Schedule Rating Coal Mines in Pennsylvania for Compensation Insurance Rates

By Rush N. Hosler,* Harrisburg, Pa.

(New York Meeting, February, 1925)

This paper was prepared for the purpose of answering some of the many questions as to why, in the construction of Pennsylvania's Coal Mine Schedule Rating Plan, various factors were, or were not, taken into consideration. Much has been written about merit and schedule rating of industrial risks from an actuarial viewpoint, therefore this phase of the question is taken up only so far as may be necessary in presenting the practical application of the plan now in use.

Companies writing fire insurance, about 30 years ago, were the first branch of insurance to use schedule rating; the values assigned their items were largely a matter of judgment. In 1913, the Industrial Commission of Wisconsin evolved the first schedule rating plan to be applied to industrial risks under compensation insurance. Pennsylvania, in 1916, with the inception of its Compensation Act, was the first state to apply the principles of schedule rating to coal mines.

A definition of the term "schedule rating" submitted by the writer in a brief to the Safety Committee of the United States Coal Commission is as follows:

> Schedule rating, as applied to compensation insurance, is an instrument to measure the hazard of known causes of accidents to which employees are exposed in industry and thereby determine an insurance rate commensurate with said hazard. It was first applied to Coal Mining in 1916 in Pennsylvania.[1]
>
> In other words, for a mine operator to insure his employees for injury under the Workmen's Compensation Act, it is necessary that he pay a certain premium based on his payroll. If all mines were assessed the same premium, it would be unfair for the mine with low natural hazard, good safety conditions, and good accident experience to pay the same premium as a mine with bad conditions and experience, therefore schedule rating was introduced.[2]

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* Superintendent, Coal Mine Section, Pennsylvania Compensation Rating and Inspection Bureau.

[1] Hugh M. Wolflin: Effects of Compensation Laws and Differential Compensation Insurance Rates on Mine Safety Conditions. U. S. Coal Com. Rept.

[2] See Report of Sub-committee on Education of Industrial Relations Committee, presented at New York Meeting, February, 1924, and published in Mining and Metallurgy, December, 1924.

To the late E. H. Downey, compensation actuary of the Insurance Department of Pennsylvania, more than to any other person belongs the credit for the great degree of refinement the Pennsylvania schedule has attained. In writing of rate regulations, Doctor Downey says:

> The processes of rate making and of risk classification and rating require close coöperation between insurers and the administrative authority charged with the supervision of insurance. The most effective agency yet devised for this purpose is the compulsory rating bureau operated by insurance carriers under public supervision. The function of such a bureau should be to establish risk classes, premium rates and rating plans, to compile statistical experience for these purposes, apply schedule and experience rating and determine the class or classes applicable to each insured establishment. To enforce compliance with bureau ratings, copies of the actual policies should be filed with the bureau and payroll audits should be reported by individual risks. The work of inspecting, rating and classifying risks, scrutinizing policies, compiling statistics, and investigating industrial processes for the purpose of erecting risk classes and devising rating plans will necessarily devolve upon the paid staff of the bureau; only the formal establishment of risk classes and class rates should be vested in representative committees of the carriers. All acts of the bureau will, of course, be subject to approval or disapproval by the administrative department of the state which has jurisdiction thereover. That this power may be intelligently exercised, the administrative authority should be represented at all deliberations of bureau committees and should be intimately acquainted with the bureau's operations and with the statistics from which rates are derived. By this means, friction between the carriers and the supervisory authority will be minimized and the public interest will be protected to the degree that the supervisory authority itself is alert and informed therein.[3]

The procedure outlined by Doctor Downey is practically the same as is provided in Section 654 of the Insurance Laws of Pennsylvania, 1921, under which the Coal Mine Section of the Pennsylvania Compensation Rating and Inspection Bureau operates. This Bureau is charged with the administration of the rating problems in connection with compensation insurance rates on coal mines in Pennsylvania. It is not a branch of the State Government, but is organized and maintained by all of the insurance companies authorized under the law to write compensation insurance on coal mines, and is subject to the approval of the Insurance Commissioner.

The most important division of the Bureau is the Inspection Committee. This is composed of well-trained mining men, representing members of the Bureau, and is presided over by the Compensation Actuary of the Pennsylvania Insurance Department. Under the guidance of this committee, the schedule has passed through successive stages of development and refinement during the past nine years. This was possible only through many meetings of all interested parties. All coal operators' associations in the state were invited to have representa-

[3] E. H. Downey, Workmen's Compensation, Chapter on Compensation Insurance, The Macmillan Co., New York.

tives meet with the Committee and coal operators have always been invited to attend the meetings. At no time, when the facts as to accident causes have been presented, has a coal operator hesitated to indorse an advanced step in the schedule taken in the interest of safety. The Inspection Committee has had the most hearty coöperation from the national Bureau of Mines and the Pennsylvania Department of Mines and their representatives have frequently sat with the Committee and have helped to solve its most difficult problems.

The educational value of the schedule is shown by its use in day and night mining schools and in the extension courses of colleges. It embodies the best extant mining practices and is more stringent in many particulars than the State mining law; for instance, its prohibition of oil lamps in any mine, of open lights in any part of a gaseous mine, fuse firing and motor-pushed trips; and its requirements for approved electric lamps as employees' lights in gaseous mines, approved magnetically locked flame safety lamps for testing purposes, clearance at room necks, credit items for additional inspection of working places daily and for thorough and effective rock-dusting for prevention of coal-dust explosions.

The requirements of the schedule are placed under specific items, which in turn are grouped under general subjects; thus the specific requirements pertaining to clearance underground are given in Item 43, which is only one item in the fourth group "Haulage Underground." The correlating of the items and groups simplifies the schedule. Although the schedule contains nine general groups with over ninety separate items, it may be said that, as a whole, the items are in but two classes:

First, those representing what may be called morale items—reflecting the morale of the operation—such as items relating to first-aid, mine-rescue facilities, and telephones. As a whole, this class includes all requirements of the schedule that cannot be tangibly measured from a statistical standpoint. No one will deny the value of first-aid or mine-rescue facilities, yet it is difficult to measure their value by a cause analysis of accidents. For this reason, the values assigned these items are judgment values, but the amounts are sufficient in each case to encourage compliance with them by a saving in the compensation insurance rate.

The second class of items are those that can be, and have been, measured by comprehensive statistics which bring out the nature of the injury, the place and cause of the accident, and its cost. In this class are found two kinds of items: those governed by natural or geological conditions and those over which the operator has the control. For example, the hazard of shaft or slope, the giving off of explosive gas, the character of roof, and the presence of draw slate are natural conditions; but the employer decides the kind of equipment used, its installation, the clearance provided, whether coal shall be undercut or blasted off the

solid, whether shots shall be fired with fuse or electric batteries, whether an adequate system of timbering shall be used, and if explosive gas is found whether the mine shall be worked with open lights or with electric cap lamps.

A brief description of the manner of compiling the information will help to a better understanding of the construction of and value assigned to the items. Insurance companies, members of the rating bureau,

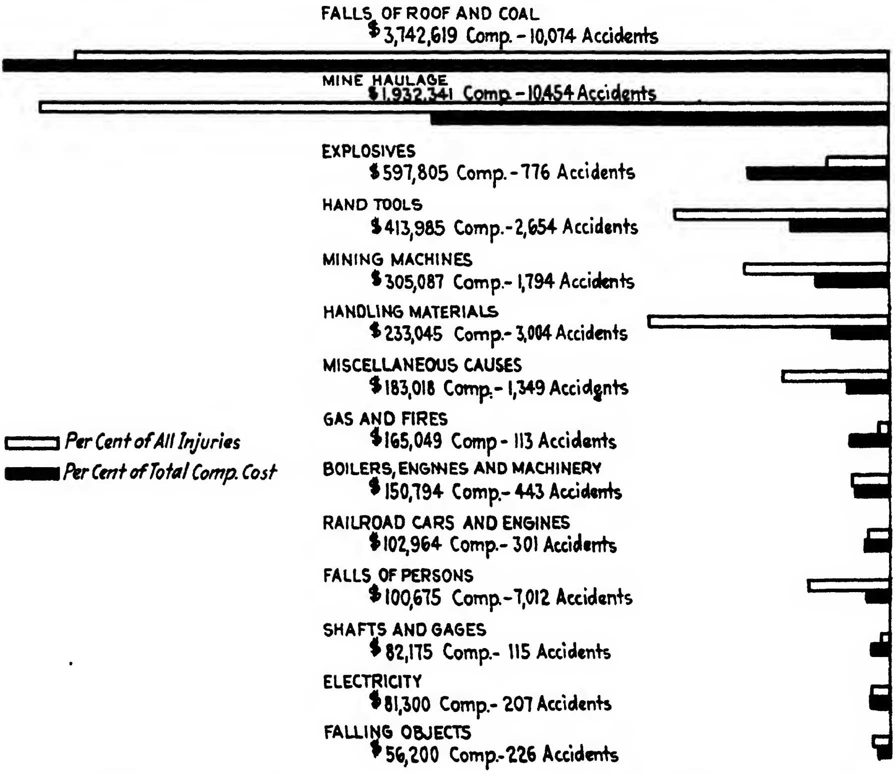

FIG. 1.—RELATIVE PROPORTION OF ALL COMPENSABLE ACCIDENTS AND OF TOTAL COMPENSATION BY CAUSE OF ACCIDENT IN BITUMINOUS MINING.

under requirements of the Department of Insurance, file a report on each accident. The report identifies the accident and, with other information, specially sets out the two most important things—the cause and the cost of each. All reports are subject to check and verification from the records of the State Department of Mines and the Compensation Board of the Department of Labor and Industry. After they are audited and evaluated, in accordance with the Act, they are coded and analyzed by nature of injury and cause, and then assigned to the particular group to which they belong. The results so obtained give the causes and total cost of each class of accidents; viz., deaths, permanent totals, major

permanents, minor permanents, temporaries and non-compensables. This is illustrated in Table 1 and Fig. 1. The aggregate cost of these different classes of accidents then becomes the basis on which the average rate for the ensuing year is predicated. To avoid too much fluctuation in rates from year to year, a 5-year period is used as a basis. For bituminous coal mining, the experience for the past five years produces an average insurance rate of $2.25 per $100 of payroll.

TABLE 1.—*Severity Distribution of Injuries by Cause of Accident,* 1918–22 *Bituminous Coal Mining*

Cause of Accident	Per Cent. of Comp. Cost	Per Cent. of Specified Injuries Attributable to Each Cause					Per Cent. of Accidents from Each Cause Resulting in Specified Injury			
		All	Death	Perm. Total	Major Perm.	Temp. Comp.	Death	Perm. Total	Major Perm.	Temp. Comp.
All Causes	100.0	100.0	100.0	100.0	100.0	100.0	3.7	0.5	2.5	93.3
Boilers, engines, and machinery	1.9	1.4	1.3	0.6	3.9	1.3	3.6	0.3	7.2	88.9
Mining machines	3.7	5.5	2.4	0.6	4.3	5.7	1.6	0.1	1.9	96.9
Shafts and cages	1.0	0.3	1.8	0.6	0.1	0.3	19.1	0.9	0.9	79.1
Railroad cars and engines	1.3	0.9	1.7	1.7	0.6	0.9	6.6	1.0	1.7	90.7
Mine cars and motors	23.7	32.2	21.8	12.9	19.6	33.0	2.5	0.2	1.5	95.8
Electricity	1.0	0.6	1.9	....	0.2	0.6	11.1	....	1.0	87.9
Explosives	7.3	2.4	4.4	24.5	12.9	1.9	6.8	5.4	13.5	74.3
Gas, dust, and fires	2.0	0.4	4.2	....	0.3	0.2	44.2	....	1.8	54.0
Falls of roof and coal	45.9	31.0	55.7	57.3	28.9	29.9	6.7	1.0	2.3	90.0
Falling objects—not roof or coal	0.7	0.7	0.9	0.6	0.2	0.7	4.9	0.5	0.9	93.7
Falls of persons	1.2	3.1	0.7	....	0.4	3.3	0.8	....	0.3	98.9
Handling materials	2.9	9.2	0.9	0.6	2.5	9.8	0.4	....	0.7	98.9
Hand tools	5.1	8.2	0.6	....	23.3	8.1	0.2	....	7.2	92.6
All other causes	2.3	4.1	1.7	0.6	2.8	4.3	1.6	0.1	1.7	96.6

NOTE.—This table covers 32,522 accidents with compensation cost of $8,147,057. Medical cost, which is not included, is $1,839,013. Of this amount $438,000 covers non-compensable accidents (less than 14 days disability prior to 1920, and less than 10 days since 1920). These non-compensable cases number approximately 50,000.

With this information all accidents are easily assigned to one of the major groups. For example, a cause analysis of the different classes of accidents shows that mine haulage, as a group, is responsible for 32.2 per cent. of all accidents. While this is more than any other cause, as to numbers, it is not true as to severity for mine haulage accidents account for only 23.7 per cent. of the insurance cost, while falls of roof and coal are responsible for 45.9 per cent. In the application of the schedule, the values assigned the items in the haulage group produce 23.6 per cent. of the total rate charges, which is equivalent to its accident cost.

The cause analysis is also made in sufficient detail to permit the breaking up of the general groups, such as mine haulage, into smaller

divisions and thus give the individual items with their values. For example, accidents caused by being squeezed between car and rib are charged to clearance; those from defective track are charged to track and roadbed; those from poor condition of cars are charged to cars; and those from motor-pushed trips are charged to this item. Penalizing of motor-pushed trips has often been adversely criticized. That the practice of pushing trips is to be condemned is amply justified by the fact that approximately 2 per cent. of the insurance cost is from motor-pushed trips and 2.2 per cent. of the total rate charges is from the item prohibiting this practice.

From time to time, many excellent suggestions and devices have been presented for the Committee's recommendation and approval. While the Committee encourages and invites suggestions at all times, the embodying of many of them as a positive requirement in the schedule is difficult from the inability to measure their value by an accident cost that their adoption and use would have prevented. Also if their value could be measured and definitely assigned, the credit allowable might prove to be so small that to require their use would involve an expenditure of money out of all proportion to the decrease in risk, so as to make it unreasonable. Again, to embody many of these suggestions in the schedule would tend toward a multiplicity of charges that might rightly be termed technical or trivial and, therefore, annoying to the operator when embodied in the make-up of his rate. To illustrate, the designer and patentee of a frog for a mine turnout or switch claims for its use additional safety. There is merit to his claim, but to require its use on the ground that it is safer than others and make a charge for its non-use cannot be justified and will involve a large expense for the new switches without an equivalent rate reduction being possible. It is clear, however, that many devices and practices are to be commended and have their place in actual use that cannot be evaluated in the schedule. The most successful safety engineers and operators in accident-prevention work are not content to stand on the requirements of the schedule, but have gone far beyond, with the one thought of obtaining the things best adapted to suit the individual operation that conditions may not only be safer but the safest possible.

In the practical application of the schedule, the Bureau Inspectors, who are trained mining men with the minimum qualifications of a first-grade mine foreman, make a complete survey of every part of the operation, paying particular attention to all places where men work. This survey is embodied in a report covering every requirement of the schedule and brings out the conditions that are in compliance therewith as well as those that are not. These reports become permanent records and copies are furnished the insurance company, which transmits them to the operator with recommendations for correcting the substandard

conditions. From these reports, the rate charges on the individual mine are developed; to which the fixed minimum is added to produce the schedule rate.

This fixed minimum may be changed from year to year, depending on the aggregate experience of the state and the average charges developed on all mines. It presupposes conditions as nearly perfect as it is possible to obtain and that which is recommended by the standards. The absence of these recommended practices is what determines the item charges. Thus again it is seen that the schedule rate is built upward from the minimum by adding the item charges and not downward from a possible maximum rate. To illustrate, if the survey finds all recommended practices under "Class IV—Haulage Underground" absent, it would add 67 cents to the minimum. If these recommended practices are made standard, the 67-cent charge would not apply and a corresponding saving could be effected.

This paper would not be complete without a reference to the objects of schedule rating. The first object, as intimated in the definition, is that it must fairly reflect the difference of hazards that may exist between risks of the same classification; that is, mines having different hazards develop rates commensurate with the hazards peculiar to each. That this object is accomplished is evident by the fluctuations in the rates of individual mines. For example, mines in the same locality, working in the same seam of coal, with natural conditions and other contributing causes alike, have a difference of more than $1.00 in their insurance rate. Some bituminous coal mines' schedule rate is as low as $1.35 while others are as high as $3.50 although the average for all in the state is only $2.25 per $100 of payroll.

The second object of schedule rating is to stimulate accident prevention. To accomplish these results, the schedule must be established from an accurate, detailed, and comprehensive statistical basis; that this has been done has already been shown. That the application of the schedule stimulates accident prevention is evident by the fact that the mines having the lowest accident record are those having the lowest rates. A group of bituminous mines, located in a district where the natural conditions are most favorable, and operated by the same company, prior to 1921, were producing approximately 450,000 tons of coal for each fatal and permanent total accident. From a tonnage standpoint, this is an enviable record as the average for the state during this same time (1916–20) was only 355,000 tons per fatal accident. During this time, this particular group of mines had on the average schedule charges in excess of $1.20. In 1920, an effort was made to comply with the schedule and everything within the control of the operator was made standard and kept so at all times; the schedule charges, as a result, were reduced to less than $0.10. The accident record during the past four years

has been one fatal accident and few temporary ones though over 5,000,000 tons of coal was produced. Similar results have been obtained by other operators who have eliminated conditions known to have caused accidents in and about mines. The bituminous mines in Pennsylvania to which the schedule is applied (representing about 60 per cent. of the production) have steadily decreased their fatal accident frequency in a greater degree than those mines to which the schedule is not applied.

The examination of the figures showing the reduction in insurance rates brought about by complying with the schedule requirements shows that accident-prevention work should be just as important a cog in the managerial machine of an operator as any other phase of their problem. It reflects itself on the cost sheet and is as much of an engineering accomplishment as a saving brought about by the introduction of improved methods or equipment.

Rate supervision, as in Pennsylvania, through the application of the schedule has been criticized because it restricts competition. Competition may be restricted to salemanship and service, but that is the crux of the whole problem. The Bureau, the agency applying the schedule, is interested only in the facts existing at the time of the survey, as reflected by the schedule. The competition in service rendered, between the different insurance companies and kinds of insurance, is a greater stimulant to accident prevention than where the insurance is under a monopolistic plan.

Much credit should be given the insurance companies for their interest and leadership in accident-prevention work. There is frequent criticism that their only interest in mine accidents was the return expressed in premium income. As mines with high accident cost have high insurance rates, insurance companies may make more money from such mines with their high rates than from mines with low accident cost and low rates.

A criticism, aimed not so much at the schedule itself as at its plan of operation, is that its application is confined to those mines that have their liability, under the Compensation Act, insured with casualty insurance companies. It is not applicable to those mines whose owners have been granted permission to carry their own liability. Compensation is for the benefit of the employees and not the employer, and for this reason is required by law. As the State requires compensation to those injured in its industries, the interest of society at large demands that those who are unfortunate enough to become its beneficiaries shall be insured of their benefits; therefore, employers should not be left to their own devices in insurance. No employer should be permitted to assume his own liability under the Act unless he has qualified under the Insurance Laws of the State in the same manner as prescribed for insurance companies.[4]

[4] Insurance Laws of Pennsylvania, 1921.

If this were done, the schedule would be applied to all mines. Safety engineers agree that the greatest single factor in the interest of safety in our coal mines that could be brought about would be to extend the plan of schedule rating as applied in Pennsylvania to all coal mines.

Perfection is not claimed for the schedule. That it accomplishes what is intended of it, there can be no doubt. Its greatest appeal is to those who are not comparing the cost of its compliance with the results that may be obtained, but to those who never think of comparing life and limb to dollars and cents, for accident prevention work may be measured in the same degree as the employer's responsibility and regard for the life and limb of his employee.

DISCUSSION

E. A. Holbrook, State College, Pa.—Two years ago a number of us worked for the U. S. Coal Commission on the subject of coal-mine accidents and we spent several weeks investigating compensation insurance as applied to coal mines in the different states. After a careful comparison between the methods of Pennsylvania and of some other states, especially those having monopolistic insurance, we came (as a body representing the employees, employers, and general interests) to the conclusion that the Pennsylvania plan as just outlined for you was the most effective method we had seen or which had been in use, at least in this country.

I call particular attention to its statistical basis. In the long run, the compilation and use of a statistical basis as a means of finding out what our accidents are and for building up preventive measures will have much greater benefit than the use of individual judgment alone.

W. W. Adams, Washington, D. C. (written discussion).—Schedule rating of coal mines makes possible a threefold accomplishment: It insures an equitable distribution of insurance cost among causes of accidents in proportion to the responsibility of each cause for the injury or death of employees; it reveals the relative importance of the various accident causes as objects to be attacked in accident-prevention work; it makes possible an annual or other periodic adjustment of cost or responsibility commensurate with actual developments in the increase or decrease of specific hazards.

Every specific "cause" of accidents may be considered a contributor to the general toll of lives lost or injuries sustained. Therefore it is eminently fitting that each contributor to the loss from accidents be required to contribute proportionately to the cost of accidents. Equity also requires that there shall be kept an "account" under the name of each "cause," and that the account be debited with losses rightfully chargeable

thereto, so that the subsequent year's contribution toward the total insurance premium may be lowered or increased according to whether the cause shows an improvement or retrogression, as compared with its previous year's record. Moreover, if a specific cause or hazard has been partly or completely eliminated, the part eliminated should no longer be charged with any portion of the insurance cost, and the cost thereafter should be spread over the remaining causes according to their respective responsibility for losses thereafter sustained.

This leads to the basic reason for schedule rating as between separate mines. Mines free from specific hazards should not be charged a premium based on hazards that exist only in other mines. Mines should pay only for hazards actually existing therein, and should be freed from the payment as quickly as the hazards are removed. This is made possible by schedule rating. Under the system of schedule rating, no mine is required to pay for hazards existing in other mines and from which its own record is clear.

Because mining operations will always be attended by accidents due to hazards inherent to the industry, or due to causes that are difficult or impossible to definitely classify, the basic insurance premium should be the average cost of the accidents in all mines in a state or other large area or group. This will insure the covering of unknown or unmeasurable hazards. With this basic premium determined, and perhaps adjusted annually to fit changing conditions, each applicant for insurance may be credited or debited with the absence or presence of specific hazards, and thereafter accordingly pay a premium lower or higher than the average for the entire state or area or group. The greatest possible number of mines should be represented in the establishment of the basic rate, thus bringing into play the law of averages and insuring the development of a stable and equitable base. Too small a number of mines may make the base rate too high or too low, with resulting inequity in credits or charges to individual policy-holders. The most equitable distribution of losses in coal-mining operations is more and more nearly attained with every increase in number of mines represented in the development of the base rate, and the permanence or continuance of the equitable distribution as regards any given policy holder, and as regards all policy holders collectively, will follow as a matter of course in the constant adjustment of the losses among known causes of accidents to meet the progress and advancement made in the constant attack against specific classes of hazards.

Application of Gaussian Curve to Mining Industry

By Hugh Archbald, E.M., Philipsburg, Pa.

(New York Meeting, February, 1925)

It is possible to construct a simple diagram of the earnings, or the production, of the men employed at a coal mine that will show not only if the conditions tend toward contentment among the men, but if the operating distribution of the work is correct. As earnings are the greatest cause of discontent, even exceeding all the other causes, if contentment exists in the matter of earnings, the likelihood of other discontents flaring up is greatly lessened.

The basis of such a diagram would be the Gaussian curve of the normal variation in human ability. Such a curve has long been recognized. H. L. Moore,[1] in discussing the quantitative relation between wages and ability says: "It has been pointed out that industrial efficiency is dependent upon physical, mental, and moral qualities, and these qualities . . . there is good reason for regarding as being distributed according to the Gaussian law.

Table 1.—*Men in Each Weight Group from* 90 *to* 190 *Lb.*

(Data for 223,690 drafted army recruits, 1917–18)

Group Weights	Number of Men	Per Cent. of Total Number of Men	Group Weights	Number of Men	Per Cent. of Total Number of Men
90–94	163	0.07	140–144	25,130	11.23
95–99	794	0.36	145–149	21,275	9.52
100–104	2,333	1.04	150–154	17,704	7.92
105–109	5,215	2.33	155–159	13,124	5.88
110–114	8,270	3.70	160–164	9,702	4.33
115–119	12,034	5.38	165–169	7,105	3.17
120–124	16,884	7.55	170–174	4,802	2.14
125–129	21,360	9.55	175–179	3,090	1.38
130–134	24,882	11.13	180–184	2,109	0.94
135–139	26,296	11.77	185–189	1,418	0.63
				223,690	100.0

[1] "The Law of Wages." Chap. IV. N. Y., 1911. The Macmillan Co.

"Industrial ability—general capacity and energy—is distributed according to the normal or Gaussian law."

An example of this variation between human beings can be found in the weights of men drafted into the army during the war, shown in Table 1. The weights varied from a very few men who weighed 90 lb. to a very few who weighed 200 lb. The number of men found in any class of 5-lb. variation progressively increases up to the class of those who weighed from 135 to 139 lb.; then the numbers found in any class progressively decreases up to the maximum weight.

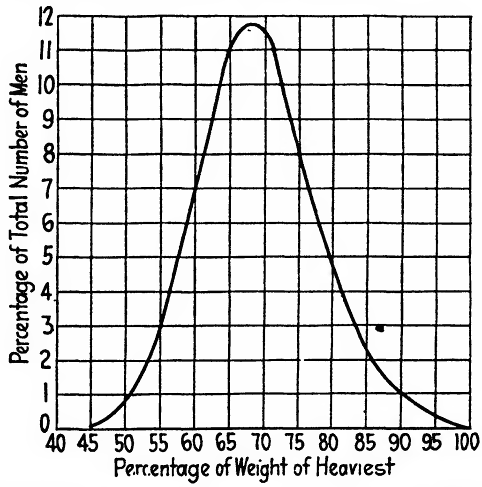

FIG. 1.—GAUSSIAN CURVE OF NORMAL VARIATION IN HUMAN WEIGHT, BASED, ON THE WEIGHT OF 223,690 DRAFTED MEN.

Were these variations in weights plotted with the weight intervals placed equally along a base line and the number of men, or percentage of the total number, plotted as an ordinate, the curve resulting from connecting the ends of the ordinates would be a Gaussian curve, Fig. 1.

It needs to be noticed in this curve of weights that there are no men who weigh nothing; moreover the practical maximum is 200 lb. The group with the least weight (the 90 to 94 lb. inclusive) have a weight that is practically 46 per cent. of the maximum. The median line of the total number of men falls at a point about 69 per cent. of the maximum weight. This median line occurs at practically the same point in any one class of men. Between classes such as intellectual workers and common laborers, the median line, of course, would not have the same value.

The point of the median line corresponds fairly closely with the median line in the mutual estimation of the ability of army officers that took place during the war, based on the army rating methods. It was then said that the average ability of officers was about 70 to 73 on a scale of a possible 100; it was a very exceptionally good man who received a

rating as high as 90 and an exceptionally poor man who was rated at 50 or less.

Various investigators have attempted to make a numerical division of 100 men. Professor Moore gives a distribution of a possible standard population of 100 men as to the numbers of men falling into each class from the highest to the lowest, the figures for each class being, 1, 1, 1, 3.5, 4.5, 7, 9, 11, 12, 14, 13, 10, 6, 4, 2, 1 (total 100). From the variations in the weights of the drafted men, a similar distribution can be made, as follows, 1, 1, 2, 2, 3, 5, 6, 8, 10, 12, 12, 11, 9, 7, 5, 3, 2, 1 (total 100); see Table 2.

TABLE 2.—*Separation of 100 Men According to Variation in Normal Human Ability, According to Calculations Based on Weight of Men Drafted into U. S. Army*

Group Rating; Percentage of Maximum	Number of Men in Group of 100	Adjusted Number of Men in Group	Group Rating; Percentage of Maximum	Number of Men in Group 100	Adjusted Number of Men in Group
100.0			72.5	10.1	10
97.5			70.0	11.5	12
95.0			67.5	11.7	12
92.5	0.7	1	65.0	10.8	11
90.0	1.0	1	62.5	9.4	9
87.5	1.6	2	60.0	7.0	7
85.0	2.3	2	57.5	4.7	5
82.5	3.4	3	55.0	2.9	3
80.0	4.7	5	52.5	1.7	2
77.5	6.4	6	50.0	0.9	1
75.0	8.3	8	47.5	0.4	

APPLICATION OF VARIATIONS TO COAL MINING

These variations can be applied to any industry but are particularly applicable to coal mining; for the work of coal mining is fairly uniform in character and requires as much strength as anything. A great variety of the classes of men is not employed, so that one can expect to find only the normal variation as it exists between men in one class. As strength and weight in all probability vary together, the normal variation between the men in a mine should correspond closely to the variations in weights found in the draft.

As examples of correspondence to the Gaussian curve, Figs. 2 and 3 and Table 3 are given. Fig. 2 and the table are from an individual coal mine in Ohio; Fig. 3 and Table 4 are from the statistics of earnings gathered by the last Coal Commission in the anthracite and bituminous industry. The figures for the Ohio mine are for the amount of coal

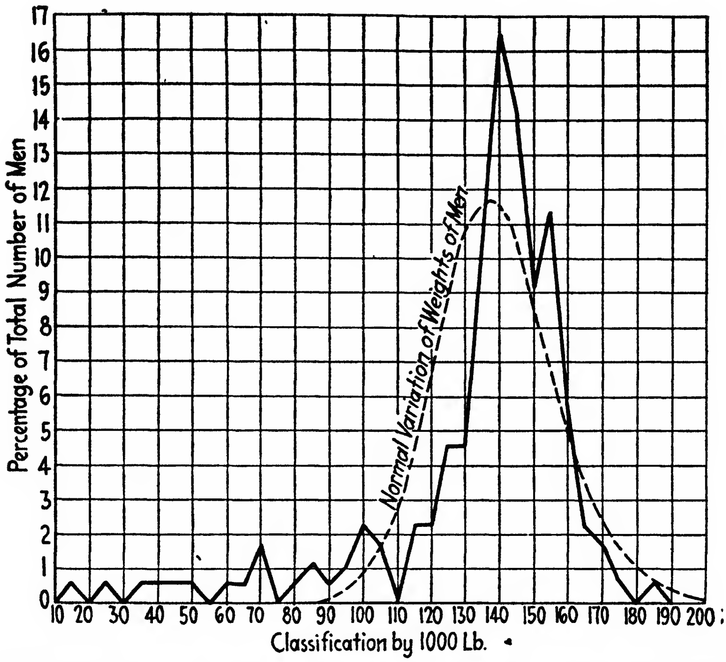

FIG. 2.—COMPARISON BETWEEN THE AMOUNT OF COAL LOADED BY INDIVIDUAL MINERS AT AN OHIO MINE AND THE GAUSSIAN CURVE OF NORMAL VARIATION IN THE WEIGHT OF MEN.

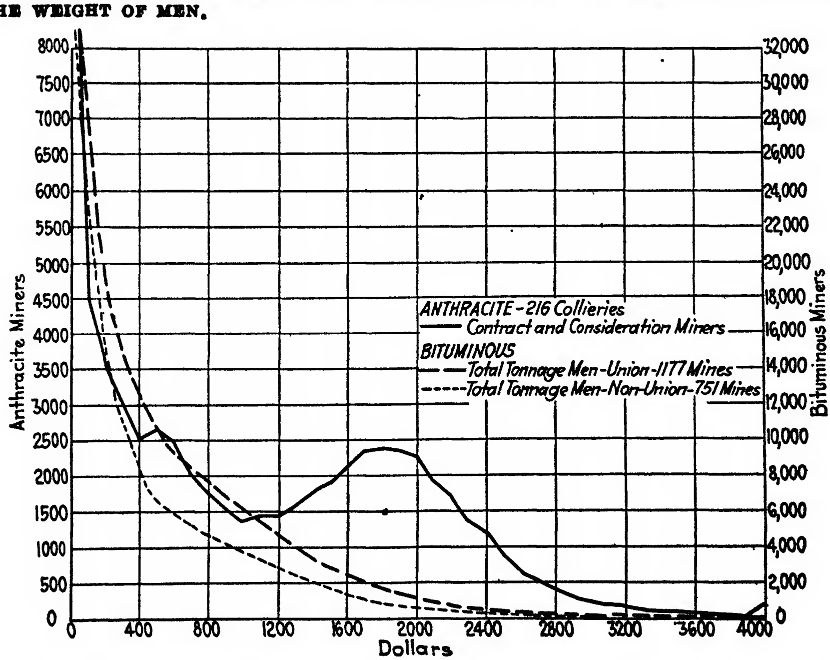

FIG. 3.—NUMBER OF MEN ON PAYROLL, SHOWN BY EARNINGS CLASSES FOR CONTRACT MINERS IN ANTHRACITE AND ALL TONNAGE MEN IN BITUMINOUS MINES, IN 1921.

produced by the individual miners and not the earnings; as the miners are piece workers, the earnings would closely correspond to the production. The mine was operating under the equal-turn clause of a union agreement and the figures were taken from a check weigh sheet and cover twelve days of work in one two-weeks period.

In tabulating the material, a classification was made with variations of 5000 lb. and the number of men counted whose output for the twelve days of work fell into each class. It was then a simple matter to calculate the percentage of the total who fell into each class. One man loaded 184,500 lb. of coal in the twelve days; the next best man loaded 176,200 lb. Then there came three who loaded a total of 516,100 lb., or an average of 172,033 lb. The number who fell into any one class progressively increased, with one exception, up to 29 men who fell into the 140,000 to 145,000-lb. class. From that high point, the numbers progressively decreased down to a couple who had worked the full twelve days and an odd number who represent changes in the working force. There was a total of 176 men on the sheet for the two weeks period. For the sake of comparison with a theoretical, objective standard curve of a hundred men, the numbers in each class were reduced to percentages.

TABLE 3.—*Classification of Men at an Ohio Mine, According to Amount of Coal Loaded in 12 Days of Work*

Classification by 1000 Lb.	Number of Men	Hundred-weights Loaded in 12 Days	Per Cent. of Total Number of Men	Classification by 1000 Lb.	Number of Men	Hundred-weights Loaded in 12 Days	Per Cent. of Total Number of Men
195				90	1	916	0.57
190				85	2	1,760	1.14
185	1	1,845	0.57	80	1	844	0.57
180				75			
175	1	1,762	0.57	70	3	2,177	1.70
170	3	5,161	1.70	65	1	683	0.57
165	4	6,665	2.27	60	1	649	0.57
160	10	16,264	5.62	55			
155	20	31,477	11.36	50	1	523	0.57
150	16	24,366	9.09	45	1	496	0.57
145	25	37,048	14.20	40	1	417	0.57
140	29	41,437	16.48	35	1	392	0.57
135	19	26,194	10.81	30			
130	8	10,561	4.55	25	1	267	0.57
125	8	10,217	4.55	20			
120	4	4,910	2.27	15	1	154	0.57
115	4	4,726	2.27	10			
110				5			
105	3	3,224	1.70				
100	4	4,101	2.27		176	241,242	100.0
95	2	1,955	1.14				

A diagram drawn on the basis of classification and percentages, as in Fig. 2, will follow approximately the Gaussian curve. When making a comparison with a standard curve, the high point of the curve was made to correspond with the standing of the man who had loaded the largest amount of coal. When it is noticed that this highest man only loaded 184,500 lb. in twelve days, or an average of 7.69 short tons a day, two questions promptly occur: (1) Whether, the total output remaining the same, a greater tonnage per man could not have been obtained with fewer men, thereby saving equipment in mine cars, rails, etc., and at the same time having less area to supervise; (2) with the improvement of some other factor, such as transportation, whether there could not have been obtained a larger output for the same number of men. In both cases, the earnings of the group employed would have been increased and costs reduced; 7.69 short tons per day is not a large output for the best men usually found in the mines. The grouping, however, of the outputs and probable earnings of the men in this Ohio mine will tend toward contentment of the mass; for there is not a wide divergence between men and the grouping is natural.

In a paper on the Earnings of Miners, by Miss Anne Bezanson,[2] is a chart, Fig. 3, which shows that the earnings of contract miners in anthracite have a partly Gaussian character. This chart, however, does not represent the full year earnings of men but the number of men whose earnings, as long as they were carried on any payroll, fell into certain classes. The chart gives the curve for contract miners in anthracite mines and the tonnage men for both union and non-union bituminous coal mines.

The chart shows: "that the bulk of contract miners, when one takes the number of men by earnings intervals, is in the intervals above $1000; whereas, in the bituminous industry the massing is in the lower earnings intervals, and the curve slopes off gradually, containing fewer men as the higher earning groups are reached.

"The anthracite curve, on the contrary, decreases gradually in the number of men involved in each interval to $1000, and then begins to increase, reaching a high point at about $1800 to $1900. Even if the year 1920 is taken for the bituminous industry, instead of the inactive year of 1921, the curves show the same general outline, although the numbers in the higher earnings classes are then more significant.

"For the year 1921, the average time worked by contract miners in anthracite was about 250 days. The average earnings for that year was between $1900 and $2000—to be exact $1922."

This chart shows that in the anthracite fields, where there is relatively steady operating time for all mines, the normal variation between men

[2] Assistant Director, Department of Industrial Research, Wharton School; published in *Annals* Am. Acad. Polit. and Soc. Sci., of Philadelphia (January, 1924).

has a chance to be developed in the earnings. In the bituminous fields, there is no intimation of any Gaussian curve. One can account for this through the fact that, as it covers a larger number of mines, there is more variation between the operating time of mines and so no chance for the normal variation to come into play.

Discontent with earnings lies on the low side of any median line. In the case of the contract miners in the anthracite field, the discontent lies on the low side of $1922; when it has dropped to some low point, such as $1000 a year or $4 a day, the discontent is great enough to induce the men to move from mine to mine in search of better opportunities for earnings. Labor turnover is undoubtedly the cause for the number of contract miners, shown on the chart, as earning below $1000.

It is this low earning point that is the danger point that should be watched in operation. Those whose earnings are around this point may be workmen of little natural ability or they may be workmen of some ability working under poor conditions. In the first case, the man may be too poor to be wanted on the job; in the second case, the conditions of work should be improved. The danger is that if any number of the men, on account of the organization or lack of proper organization of the work, are suffering from any such condition as unemployment within employment, and consequently are not earning a satisfactory wage, their discontent will induce the whole body of men to try to obtain higher rates of pay. Rates of pay should, of course, not contain any element of reward for avoidable unemployment. When rates do contain such an element, the effect is spread over the whole body of rates and the cost of operation is seriously increased.

The third point to notice concerning the enumeration of the contract miners in the anthracite mines, according to their earning classification, is that if the median line of $1922 is taken at the theoretical percentage of 68, the best men should be earning $2826 a year. The chart shows that only about 1 per cent. of the men actually earn this amount and that on the high side of the median line there is a correspondence with the Gaussian curve. As many thousand men are considered in this chart, it is only natural that a few super-excellent men should be found earning more than this amount.

On the low side of the median line, theoretically the number who earn less than 46 per cent. of the maximum should be negligible. The earnings for the men of the very poorest natural ability should be $1100; The chart records a larger number of men than should be found in this class.

In contrast to these two instances showing a correspondence between facts and a theoretical Gaussian curve, two analyses are given from a company mining bituminous coal that has had much labor trouble in the past and has made strenuous efforts to establish labor relations such that it may have contentment among the men employed. It had not,

however, studied the organization of the underground work, an investigation of which disclosed much discontent though little outflaring.

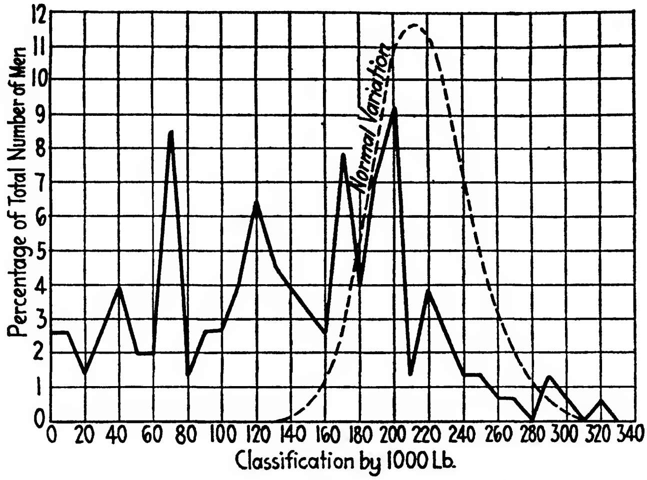

FIG. 4.—COMPARISON BETWEEN AMOUNT OF COAL LOADED BY VARIOUS PERCENTAGES OF MINERS AT A PITCH MINE AND GAUSSIAN CURVE OF NORMAL VARIATION IN WEIGHT OF MEN.

The general manager of the company claimed no more than that the underground work was conducted the same as the average coal mine. The data were gathered from the company weigh sheets and the calcula-

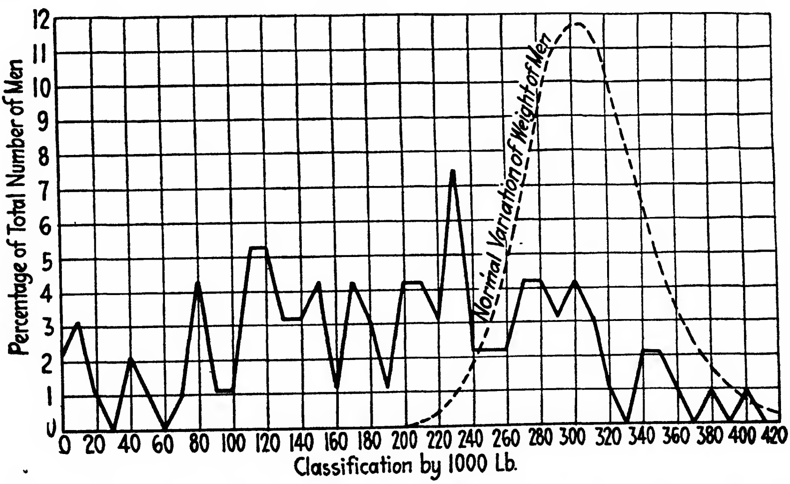

FIG. 5.—COMPARISON BETWEEN AMOUNT OF COAL LOADED BY VARIOUS PERCENTAGES OF MINERS AT A MACHINE MINE AND GAUSSIAN CURVE OF NORMAL VARIATION IN WEIGHT OF MEN.

tions made in the same manner as for the Ohio mine, with the addition that in these cases the earnings were compared to the outputs and are known to correspond. Tables 4 and 5 and Figs. 4 and 5 show that there

is not even an intimation of similarity in the results obtained from the men to any theoretical Gaussian curve.

TABLE 4.—*Classification of Men at a Pick Mine According to Amount of Coal Loaded in* 14 *Days of Work*

Classification by 1000 Lb.	Number of Men	Hundred-weight Loaded in 14 Days	Per Cent. of Total Number of Men	Classification by 1000 Lb.	Number of Men	Hundred-weight Loaded in 14 Days	Per Cent. of Total Number of Men
330				150	5	7,824	3.28
320	1	3,218	0.66	140	6	8,592	3.94
310				130	7	9,465	4.60
300	1	3,041	0.66	120	10	12,355	6.57
290	2	5,841	1.31	110	6	6,843	3.94
280				100	4	4,242	2.62
270	1	2,797	0.66	90	4	3,866	2.62
260	1	2,632	0.66	80	2	1,751	1.31
250	2	5,137	1.31	70	13	9,887	8.56
240	2	4,847	1.31	60	3	2,022	1.97
230	4	9,507	2.62	50	3	1,616	1.97
220	6	13,517	3.94	40	6	2,615	3.94
210	2	4,387	1.31	30	4	1,721	2.62
200	14	28,536	9.22	20	2	514	1.31
190	11	21,497	7.25	10	4	679	2.62
180	6	11,136	3.94	0	4	296	2.62
170	12	19,247	7.90				
160	4	6,559	2.62		152	216,187	100.0

It is possible, also, by using the Gaussian curve to construct an objective standard for the output that should be obtained from any number of men employed on coal. In the case of the machine mine given in Fig. 5, the best man loaded an average of 14.3 short tons per day. If 14 tons is taken as the standard for a good miner, who would average 92.5 per cent. of any maximum, the amounts that should be obtained from those of different ability can be set down, as the numbers who should be found in each group are known and the average loading capacity of each group is a proportion of the maximum. This has been done in Table 6. The total tonnage per day that should be obtained from 100 men of varying ability with this maximum, is 1046 short tons. As only 95 men were employed in this machine mine, 95 per cent. of 1046 tons, or 993 tons, can be taken as the standard that should have been obtained. Actually over these 14 days the mine averaged 678 short tons per day so that the performance was two-thirds of the objective standard.

TABLE 5.—*Classificaton of Men at a Machine Mine, According to Amount of Coal Loaded in* 14 *Days of Work*

Classification by 1000 Lb.	Number of Men	Hundred-weight Loaded in 14 Days	Per Cent. of Total Number of Men	Classification by 1000 Lb.	Number of Men	Hundred-weight Loaded in 14 Days	Per Cent. of Total Number of Men
400	1	4,002	1.05	180	3	5,518	3.16
390				170	4	7,098	4.24
380	1	3,877	1.05	160	1	1,698	1.05
370				150	4	6,066	4.22
360	1	3,664	1.05	140	3	4,377	3.16
350	2	7,131	2.10	130	3	4,046	3.16
340	2	6,954	2.10	120	5	6,386	5.27
330				110	5	5,641	5.27
320	1	3,288	1.06	100	1	1,080	1.05
310	3	9,521	3.18	90	1	908	1.05
300	4	12,209	4.22	80	4	3,353	4.22
290	3	8,843	3.18	70	1	716	1.05
280	4	11,350	4.22	60			
270	4	11,030	4.22	50	1	523	1.05
260	2	5,298	2.11	40	2	889	2.11
250	2	5,078	2.11	30			
240	2	4,953	2.11	20	1	234	1.05
230	7	16,307	7.37	10	3	367	3.18
220	3	8,831	3.16	0	2	62	2.10
210	4	8,587	4.22				
200	4	8,044	4.22		[95	189,839	100.0
190	1	1,930	1.05				

TABLE 6.—*Calculation for an Objective Standard Output for* 100 *Men, When Best Man Can Average* 14 *Short Tons per Day*

Group Rating	Number of Men	Average Output Per Day	Total Output for Group	Group Rating	Number of Men	Average Output Per Day	Total Output for Group
92.5	1	14.0	14.00	67.5	12	10.206	122.47
90.0	1	13.6	13.60	65.0	11	9.828	108.11
87.5	2	13.23	26.46	62.5	9	9.450	85.05
85.0	2	12.85	25.70	60.0	7	9.072	63.50
82.5	3	12.47	37.41	57.5	5	8.694	43.47
80.0	5	12.096	60.48	55.0	3	8.316	24.94
77.5	6	11.718	70.30	52.5	2	7.938	15.87
75.0	8	11.341	90.72	50.0	1	7.560	7.56
72.5	10	10.962	109.62				
70.0	12	10.584	127.00				1046.26

Application of Gaussian Curve to Other Industries

The Gaussian curve can be used, of course, in any industry. For instance the earnings of the employees in a shop manufacturing men's clothing were found to have this character. It was not the result of a conscious effort on the part of the management of the shop to have the earnings so conform, but rather the result of good handling of the work in process. At the same time, the management of this shop was envied by those operating other shops in the same city for the reason that it could get its people do what it wanted, while the other shops were continually having labor troubles. The earnings in the other shops did not show any normal variation in ability.

In conclusion, it needs to be admitted that the construction of such diagrams as are here presented are not of great value if there is much intermittency in the operation of a mine. If a mine is only operating a few days in a month, there is likely to be a good deal of labor turnover in that men will shop around seeking work. During a period of steady work, labor turnover may at first spoil the best value of such diagrams; but the attempt to follow the facts shown by these diagrams is likely to decrease the turnover. The main value of drawing such diagrams is that they set an objective standard toward which to work and a measure of accomplishment.

DISCUSSION

Donald A. Laird.—The data do not give a fair picture of individual differences. Some of the miners worked twelve full days and their output for twelve full days was measured. Other miners worked only one-half day or two days, but in the distribution table they are given the same importance as the miners who worked full time. In other words, to get at these differences in ability, the output per unit of time worked should be considered. Doubtless, had the author been able to get records of the time that these men had been engaged in the mines, practically all of the data would have come very close to a normal distribution curve. The output of a miner depends not only on his strength but on some mental factors, which perhaps the psychologists tend to overemphasize. I can see where the spirit, or morale, or loyalty of the workman has a great deal to do with his output. The fact that a miner is married will make him turn out more product than the man who is single. In the case of insurance solicitors that holds true; the married solicitors are better. Twelve companies now give preference to the married men. It may be that when the single man gets married he will work harder; that is a matter of motivation.

I can also see how certain factors of this normal distribution of mining ability might be influenced. One miner, whose work is 6 ft. from the car,

takes two or three steps with every shovelful; another miner takes two or three minutes to adjust his work so that he can do it without taking those steps. As the normal distribution affects the miners as every one else, there is presumably a normal distribution in the intelligence of the miners. There are individual differences and the men who go from mine to mine claiming unfair treatment in the hands of the previous employers, poor mining conditions and so forth, very often advertise the fact that the man is at the wrong end of the distribution curve of miners. Miners should be so selected and motivated in their work that not a normal distribution, but a skewed curve, is obtained. Some time ago, the twelve insurance companies that I mentioned found that the output of their solicitors was a skewed curve, but curving toward the wrong end; that has been changed and they are now getting from one hundred solicitors more than five hundred had been able to do before.

In the case of a mine there is considerable overhead and wherever you find a normal distribution of output among miners it is brought about only by the honest and consistent and continued effort of operators, and it can be brought about and it can be and certainly is an object worth seeking.

T. T. Read, Washington, D. C.—My principal objection is to the title. The curves referred to are ordinary frequency curves, as familiar to statisticians as trowels are to masons, and it seems to me as objectionable to refer to them as Gaussian curves as it would be to refer to trowels as spatulate mortarial instruments.

Fig. 2 is so drawn that it might be inferred that there is a direct relation between the weight of men and the amount of coal they load, and that men weighing about 135 lb. load the most coal in a shift. This is not true, nor does the text claim it to be true, but Fig. 2 might easily cause the erroneous inference to be drawn.

As Fig. 3 is drawn on a different basis, it loses most of its value as a comparison. If the data were plotted on the same basis as Fig. 2, the resulting curves would probably resemble the curve of coal loaded in Fig. 2, whereas they now look quite different.

The curves in Figs. 4 and 5 indicate that something affects the output of coal loaded by groups of miners, at the mines cited, other than the natural and to-be-expected varying working capacity of the men. Without more information than is given as to the cause, or causes, of this variability, it does not seem advisable to attempt discussion of the curves, other than to concur with the last sentence of the paper, which states that the construction of such diagrams is useful as revealing whether results correspond to normal frequency, to the end, if they do not, that a further search can be made to ascertain the cause, or causes, of the unexpected variability.

Properties of Liquid-oxygen Explosives*

By G. St. J. Perrott,† Pittsburgh, Pa.

(New York Meeting, February, 1925)

During the past year, the Bureau of Mines has carried on an investigation of liquid-oxygen explosives (L.O.X.) to supplement the work described in previous publications.[1] The present paper gives results of the first part of this work, which was a laboratory investigation of the properties of typical combustibles used in L.O.X., and the relation of these properties to the absorption and retention of oxygen by the explosives and their explosive characteristics. No attempt will be made to describe the development of liquid-oxygen explosives, because this phase of the subject has been well covered.[2]

The L.O.X. cartridge consists of a paper wrapper filled with an absorbent combustible material that is saturated with liquid oxygen by soaking it therein. After saturation, the cartridge is removed from the liquid and fired with fuse and cap, or electric detonator, in a manner similar to other explosives. Certain types of cartridge may be detonated with fuse alone, requiring no cap to initiate the detonation. By suitable variation of the nature and density of the combustible, cartridges having a wide variety of explosive characteristics may be made.

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† Physical Chemist, Pittsburgh Experiment Station, Bureau of Mines.

[1] George S. Rice: Development of Liquid-oxygen Explosives during the War. Bur. of Mines *Tech. Paper* **243** (1920).

S. P. Howell, J. W. Paul, and J. L. Sherrick: Progress of Investigations on Liquid-oxygen Explosives. Bur. of Mines *Tech. Paper* **294** (1923).

[2] Richard Pabst: Flüssiger Sauerstoff und Seine Verwendung als Sprengstoff im Bergbau, München and Berlin (1917).

H. Diederichs: Die Erzeugung und Verwendung Flüssiger Luft zu Sprengzwecken, *Stahl und Eisen* (1915) **35**, 1146–1151, 1177–1181.

Michael H. Kuryla and Galen H. Clevenger: Liquid-oxygen Explosives at Pachuca. *Trans.* (1923) **69**, 271.

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Available Combustibles

It is difficult to name any oxidizable material that has not at some time been used in L.O.X. Lampblack is the combustible most widely used and which, in the present stage of development, seems best suited for most blasting operations. Other materials that have been employed are wood pulp, cork dust, charcoal, coal dust, peat, oil absorbed in kieselguhr, naphthalene, anthracene, carbene, ground straw, and powdered metals.

Life of L.O.X. Cartridge

The most important requirement of an L.O.X. cartridge is that it shall detonate with good strength at a considerable time after it has been

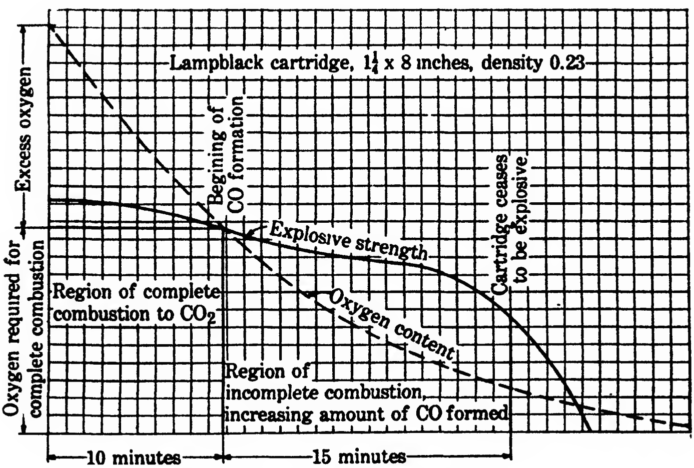

Fig. 1.—Relation between explosive strength, oxygen content, and time of evaporation; lampblack cartridge, 1¼ by 8 in., density, 0.23 gm. per c. c.

dipped. In many blasting operations, it is also essential that very little asphyxial carbon monoxide be produced. Evaporation of oxygen begins immediately the cartridge is removed from the dipping container, and continues until the cartridge is fired.

In the literature of L.O.X., the life of the cartridge is usually taken to mean the time, in minutes, that elapses between removal from the dipping container and the moment at which just sufficient oxygen remains for combustion to CO_2, H_2O, and oxides of any other elements present. The cartridge will explode, however, for a considerable time thereafter, but with the formation of increasing quantities of CO and H_2. Kuryla and Clevenger distinguish between available life (the time taken for evaporation to the CO_2 point) and explosive life.

In Fig. 1 is shown, diagrammatically, the relation between oxygen content and explosive strength of a 1¼ by 8 in. lampblack cartridge containing 0.23 gm. of combustible per cubic centimeter of cartridge. For comparison, the diagram is modeled after one in the paper by Kuryla and Clevenger, but the relative values of explosive strength as determined experimentally have been substituted for the curve given by those writers. Here, the available life before formation of CO begins is 10 min., and the explosive life 25 min. The explosive strength is at the maximum when the cartridge is removed from the dipping container, and decreases slowly and fairly regularly for 20 min., after which the strength falls off rapidly. Beyond the 20-min. period, the explosive strength does not decrease in proportion to the loss of oxygen. If a higher packing density (for example, 0.38 gm. per c. c.) is used, the cartridge after the first minute contains insufficient oxygen for complete combustion to CO_2, yet it may be fired after 25 min. evaporation with a strength at least as great as the lighter cartridge and after 10 min. evaporation with 15 per cent. greater strength. These data, for which considerable experimental evidence will be given later, indicate that where the presence of CO is not detrimental, greater explosive effect may be obtained by increasing the packing density so that, at the time of firing, considerable oxygen deficiency exists beyond that required for complete combustion to CO_2.

The time taken for evaporation of a given L.O.X. cartridge to the point where just sufficient oxygen is present for complete combustion depends on: (1) amount of oxygen initially absorbed; (2) amount of oxygen required for complete combustion; (3) rate of evaporation of oxygen from the cartridge. The first factor depends on the volume of cartridge occupied by combustible particles into which oxygen cannot penetrate, and equals $V - \frac{W}{\rho} \times 1.13$ gm., where V is the volume of the cartridge, W its weight, and ρ the true density of the cartridge material. The second factor depends on the weight of the cartridge and its oxygen factor; that is, the amount of oxygen required for complete combustion of unit weight of combustible. The third depends on: the character of the combustible absorbent material; the diameter of the cartridge; and the environment (temperature of surroundings and whether evaporation takes place in still or moving air, or the cartridge is confined in a bore-hole). Expressed mathematically, Life (in minutes) $= \frac{f_s - f_l}{e}$, where f_s is ratio of weight of oxygen to weight of cartridge when completely saturated, f_l is oxygen ratio necessary for complete combustion, and e is the decrease in oxygen ratio per minute due to evaporation. f_s can be shown to equal $\frac{\rho - d}{\rho d} \times 1.13$, where d is apparent density of cartridge,

and 1.13 is density of liquid oxygen. For a cartridge of pure carbon, such as acetylene black, f_l = 2.67; for wood pulp, 1.34; naphthalene 3.00, etc. The disadvantage of a cartridge mixture containing an inert non-combustible absorbent, such as kieselguhr, is immediately apparent because, for a given amount of combustible per unit volume, the space for absorption of oxygen is less than when no inert diluent is employed.

Factors Affecting Rate of Evaporation

Combustible Absorbent Material

The most important property of the combustible material affecting the rate of evaporation is its particle size. If the particles of a combustible, such as lampblack, are of colloidal fineness, the surface exposed per unit volume is so large that very little of the absorbed liquid is out of range of the surface forces. Hence, no liquid is lost by dripping out of the saturated cartridge and, as evaporation takes place, the liquid in the inner parts of the cartridge is not drawn, by capillarity, to the outer parts. With a combustible composed of larger particles, such as wood pulp, much of the liquid is very loosely held in droplets in the relatively large interstices between the particles. Part of the liquid drips from the cartridge immediately it is removed from the dipping container and, as evaporation takes place, a large proportion of the remainder is drawn, by capillarity, to the outer part of the cartridge and evaporation takes place at a faster rate than in the case of lampblack. Wood-pulp cartridges feel colder to the touch than lampblack cartridges, and if an absorbent paper wrapper is used, it will be wet with liquid oxygen for a considerable time after dipping, while the wrapper of the lampblack cartridges dries at once.

Table 1 gives analyses of combustible materials used in L.O.X. Table 2 gives evaporation data for a number of combustible materials, packed in 1¼ by 8 in. cartridges and allowed to evaporate in still air. The paper used for the cartridge wrapper consisted of two thicknesses of a grade of hard fiber cotton rag paper, 0.007 in. thick. Each wrapper weighed 5 gm. and required 5.4 gm. oxygen for complete combustion. For convenience in comparison, the amount of oxygen necessary for complete combustion of the lampblack cartridges has been taken as 2.4 g. per gram. of cartridge. The amount actually varies from 2.2 to 2.6 g., depending on the composition of the lampblack. The factor for coal dust has been taken as 2.39, for wood pulp 1.34, and for fuel oil 3.4, correction being made for the oxygen requirements of the wrapper in determining the oxygen value of the cartridge.

In Fig. 2 are set down evaporation curves for three typical blacks: lampblack B, a fluffy material difficult to pack; lampblack E, a material

TABLE 1.—*Analyses of Combustible Materials*

Material	H_2O, Per Cent.	Volatile Matter, Per Cent.	Fixed Carbon, Per Cent.	Ash, Per Cent.	H, Per Cent.	C, Per Cent.	N, Per Cent.	O, Per Cent.	S, Per Cent.	Heat of Combustion, Calories per Gram	Oxygen Required per Gram for Complete Combustion, Grams
Lampblack B	1.5	1.8	96.6	0.1	0.8	95.6	0.1	2.7	0.7	7,972	2.59
Lampblack C	1.2	2.9	95.9	0.0	1.1	95.9	0.1	2.2	0.7	8,061	2.59
Lampblack D	2.2	3.5	94.3	0.0	1.1	94.7	0.1	3.4	0.7		2.59
Lampblack E	2.7	13.6	83.6	0.1	1.6	89.1	0.0	9.2	0.0	7,467	2.41
Lampblack M	4.4	11.5	84.1	0.0	1.7	88.1	0.2	9.2	0.8	7,194	2.40
Gas black S	1.8	5.1	93.1	0.0	0.9	94.2	0.0	4.9	0.0	7,715	2.54
Gas black A	2.6	7.1	90.3	0.0	0.9	92.5	0.1	6.5	0.0	7,570	2.48
Gas black K	5.3	10.4	84.2	0.1	1.1	88.0	0.1	10.7	0.0	7,106	2.35
Acetylene black	0.0	0.5	99.3	0.2	0.2	99.6	0.0	0.0	0.0	7,978	2.68
Carbene	0.2	28.3	70.3	1.2	5.8	92.5	0.1	0.3	0.1	9,580	2.93
Peat	7.5	61.1	26.8	4.6	6.0	51.7	2.2	34.7	0.8	4,972	1.52
Wood pulp	8.0	80.3	11.6	0.1	6.6	47.5	0.0	45.7	0.1	4,406	1.34
Cartridge paper	4.8			6.5	6.2	39.8	0.1	47.2	0.2		1.08

TABLE 2.—*Rate of Evaporation of Oxygen from Lampblacks and Other Absorbents*

Material	Weight of Cartridge Grams	Weight of Cartridge after Soaking Grams	Time of Evaporation to Oxygen Ratio for Exact Combustion	Evaporation Period, Minutes											
				0	2	4	6	8	10	12	14	16	18	20	22
				Grams of Oxygen in Cartridge after Evaporation											
Lampblack M	29	208	15	179	157	141	125	112	100	88	76	66	56		
Lampblack M	37	208	10	171	150	134	117	104	89	78	65	56	46		
Lampblack E	28	213	12	185	158	138	119	99	83	66	54	43			
Lampblack E	34	214	9	180	150	131	111	92	74	58	46	36			
Lampblack D	52	214	4	162	140	123	108	93	78	66	52	40	31	23	18
Lampblack B	40	211	9	171	147	131	117	105	92	82	72				
Lampblack B	50	215	5	165	144	127	115	102	89	77	68	58			
Lampblack C	47	205	5	158	136	120	103	88	73	58	45	34			
Gas black K	40	213	8	173	152	132	112	94	77	64					
Gas black A	54	215	3	161	140	118	100	82	67	56	48	41			
Gas black S	59	213	1	154	132	111	93	79	66	58	51	43	38	34	30
Acetylene black	41	211	7	170	147	127	108	91	77	64	53				
Wood pulp	52	195	7	143	118	96	76	58	42						
Kieselguhr	60	223		163	145	125	108	92	74	57	45	34			
Kieselguhr plus 40 % fuel oil	83	226	3	143	119	98	80	61	43	29	20				
Kieselguhr plus 50 % coal dust	82	232	5	150	129	109	90	72	53	38	28				

easily packed; and gas black S, which had been compressed at the factory and packed easily. It will be noticed that the rate of evaporation of oxygen from lampblack B is increasingly less than that of lampblack E. This decrease in evaporation rate is typical of those lampblacks that tend to contract in volume as the oxygen evaporates. The vacant space between wrapper and lampblack, filled with cold oxygen gas, acts as an insulating layer and causes a diminution in the evaporation rate. Lamp-

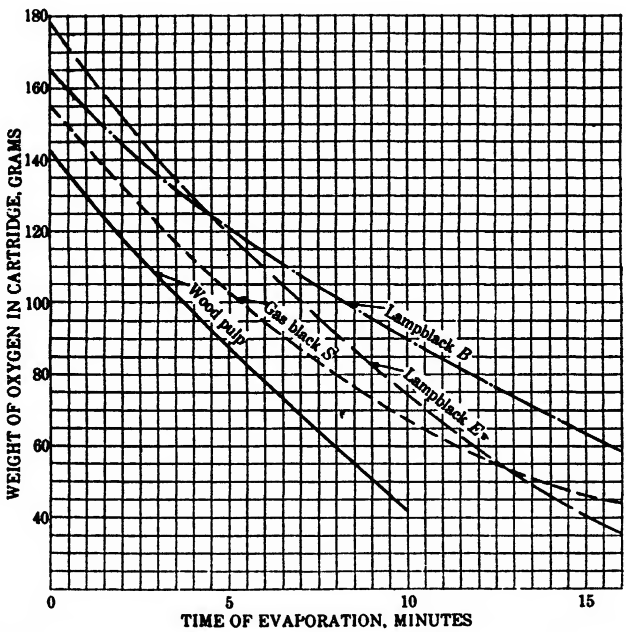

FIG. 2.—RATE OF EVAPORATION OF OXYGEN; 1¼ BY 8 IN. CARTRIDGES.

blacks of this character are fluffy and difficult to pack and, when packed, contain large pockets of occluded air. When the cartridges are soaked in liquid oxygen, the air is partly driven out and partly liquefied; and as the liquid evaporates, surface forces cause the contraction in volume. If such a cartridge is redipped, the evaporation rate is faster than before; while with easily packed lampblacks, such as E, oxygen evaporates at the same rate as after the first soaking. No relation is apparent between chemical analysis of the blacks and their behavior on packing, nor can any difference be observed under the microscope. In spite of the more favorable evaporation rate of lampblacks of type B, it is believed that lampblacks that pack easily to give a firm cartridge, such as E, are better suited for use in L.O.X. because they detonate at a uniform rate, whereas those of type B tend to give erratic rates of detonation. Gas blacks, such as S, are also in the desirable class.

Kieselguhr, Fig. 3, shows about the same efficiency as lampblacks of type E. When mixed with oil, less oxygen is absorbed initially and the evaporation rate in percentage of the oxygen absorbed is higher. The same condition exists when coal dust is mixed with kieselguhr. Wood pulp absorbs less oxygen initially than a lampblack cartridge of similar density, because of the low true density of wood pulp, and the percentage evaporation rate is higher.

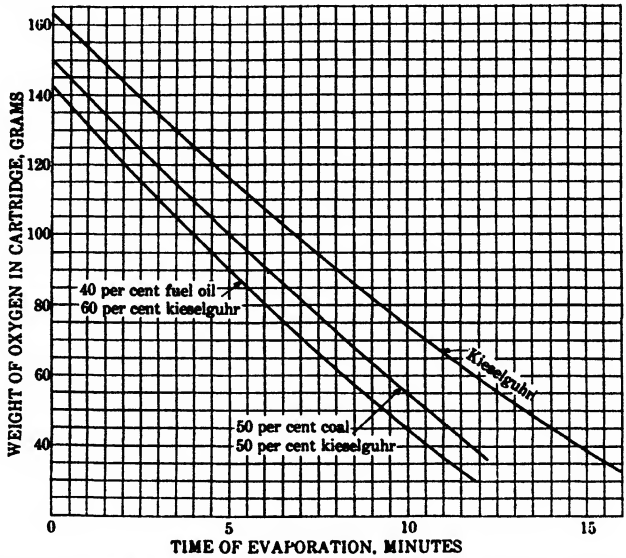

FIG. 3.—RATE OF EVAPORATION OF OXYGEN; $1\frac{1}{4}$ BY 8 IN. CARTRIDGES.

Diameter of Cartridge

The initial rate of evaporation of oxygen from a cartridge is roughly proportional to the surface exposed; or, neglecting the surface of the ends is proportional to $2\pi rl$, where l is the length of the cartridge. The weight of material in the cartridge is, however, equal to πr^2ld, where d is the apparent density or weight of cartridge per unit volume. The time, in minutes, that elapses between conditions of saturation and any other oxygen-carbon ratio is $\frac{W(f_s - f_t)}{E}$ where W is weight of dry cartridge; f_s and f_t represent weight ratios of oxygen to cartridge in saturated cartridge and at time t, respectively; E is average rate of evaporation during time t, expressed in grams per minute. For cartridges of different diameter but identical density and length, $f_s - f_t$ is identical, and the time or life to the given conditions is proportional to $\frac{W}{E}$ or to $\frac{r^2}{r} = r$. With large cartridges where the surface of the ends becomes of influence, the ratio $\frac{r}{l + r}$ may be used as proportional to life, where l is constant.

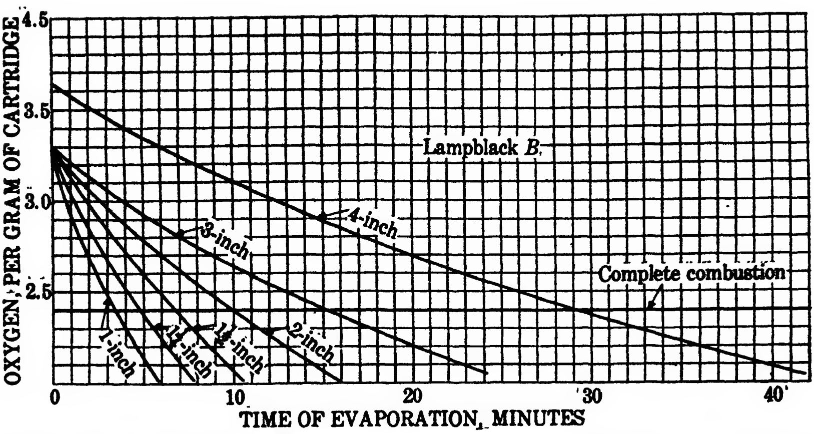

Fig. 4.—Effect of size of cartridge on evaporation rate; lampblack B.

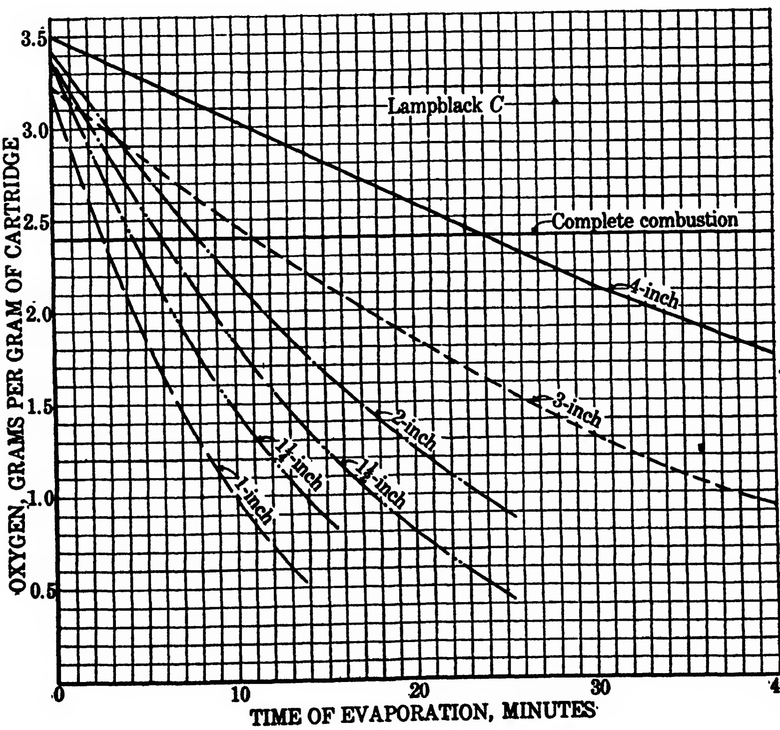

Fig. 5.—Effect of diameter of cartridge on rate of evaporation of oxygen; lampblack C.

Actually, however, while the initial rate of evaporation is roughly proportional to the diameter of the cartridge, the rate of evaporation over the life of the cartridge increases less rapidly with increased size of cartridge than would be indicated by the simple relationship: evaporation $\propto r$. This is due to the fact that, as cartridge diameter increases, the oxygen in the inner portions is insulated by an increasing layer of combustible material and cold oxygen vapor, and conduction from the outside is increasingly impeded. In Table 3 and Figs. 4, 5, and 6, are given evaporation data obtained with three lampblacks packed in cartridges from 1 to 4 in. in diameter. The data show that the life, to conditions of complete combustion, of a 2-in. cartridge is about twice that of a $1\frac{1}{4}$-in. cartridge; while a 4-in. cartridge has 2.5 to 3 times the life of a

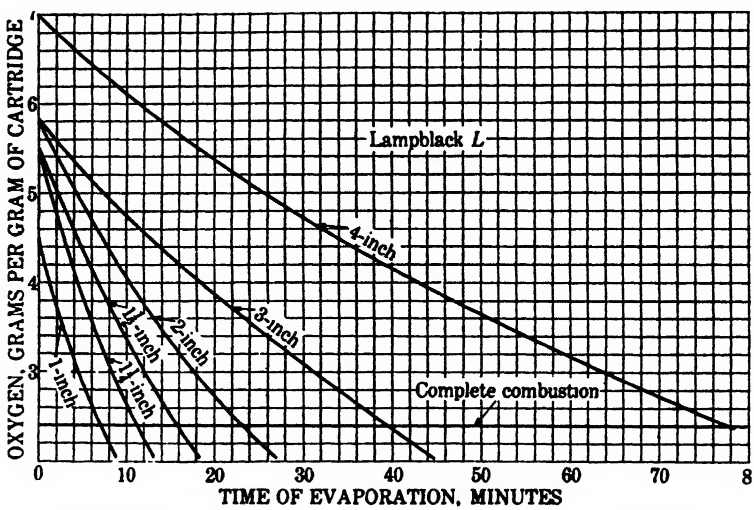

FIG. 6.—EFFECT OF SIZE ON EVAPORATION RATE; LAMPBLACK L.

2-in. cartridge. The cartridges of a given lampblack varied slightly in density, but the results indicate what might be expected in practice, for large cartridges usually pack to somewhat lower density.

Environment

Evaporation in the bore hole is somewhat less rapid than in open air, as is shown in Fig. 7. These data were obtained in a bore hole, $1\frac{1}{2}$ in. in diameter by 8 ft. long, in concrete and are averages obtained from five cartridges in the bore hole. The life to the exact combustion point is increased about 20 per cent. over that in still air, as a result of the insulating effect of the cold oxygen gas surrounding the cartridges. Evaporation in moving air is more rapid than in still air.

TABLE 3.—*Relation between Diameter of Cartridge and Rate of Evaporation; Cartridges 8 In. Long*

	Lampblack B						Lampblack C						Lampblack L					
Diameter, Inches	1	1¼	1½	2	3	4	1	1¼	1½	2	3	4	1	1¼	1½	2	3	4
Weight, dry, grams	29	50	73	125	285	481	31	47	73	123	295	471	27	31	47	75	170	275
Weight of wrapper, grams	4	6	7	8	14	23	4	6	7	8	14	23	4	6	7	8	14	23
Density, grams per cubic centimeter	0.28	0.31	0.31	0.30	0.31	0.29	0.30	0.29	0.31	0.30	0.32	0.29	0.26	0.19	0.20	0.18	0.18	0.17
Weight saturated, grams	136	215	314	540	1226	2231	137	205	314	540	1225	2131	150	204	306	511	1172	2045
Grams evaporation per minute:																		
0–10 min		7.4	9.2	11.5	19.0	26.5		8.5	10.5	14.5	20.0	24.5		8.9	9.9	13.3	19.6	24.5
10–20 min			6.4	8.0	12.5	18.5			8.1	11.8	18.4	20.5			7.4	9.3	15.1	18.5
20–30 min					11.5	15.5					16.1	21.0					12.9	15.5
30–40 min					11.3	12.5					11.0	18.0					12.2	12.5
Oxygen initially absorbed per gram of cartridge	3.69	3.30	3.31	3.32	3.30	3.64	3.42	3.36	3.31	3.40	3.15	3.52	4.55	5.57	5.50	5.81	5.90	6.43
Time at which oxygen ratio = 2.4, minutes	3	5	7	10	15	30	3	5	6	8	11	23.5	7	12	16	24	40	78

Cartridge Paper

Cartridge paper for L.O.X. should absorb oxygen readily, have good mechanical strength after soaking, and be a good heat insulator. A grade of hard fiber cotton rag paper 0.007 in. thick has been used in the present work, and was suggested to the writer by George B. Holderer of the Air Reduction Co. Non-absorbent papers, such as thin wrapping paper, have been used by several commercial organizations with success. They

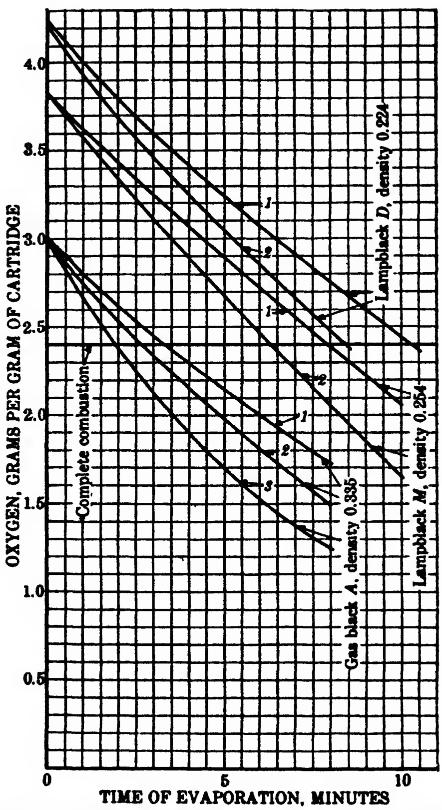

FIG. 7.—COMPARISON BETWEEN RATE OF EVAPORATION IN BORE HOLE AND IN AIR; 1, BORE HOLE; 2, STILL AIR; 3, WIND.

have the advantage of cheapness, but cartridges with such wrappers take considerably longer to saturate, as the liquid must soak in through the bottom of the cartridge. From the point of view of rate of evaporation, the absorbent papers are somewhat more efficient. Various types of insulating wrapper have been proposed, but have the common disadvantage of taking up considerable space and decreasing the strength per unit volume of cartridge. It is believed that an absorbent paper wrapper of the type used in the present work should prove most suitable for general

purposes. Table 4 shows rate of evaporation of oxygen from cartridges of lampblack E packed in different wrappers.

TABLE 4.—*Evaporation of Lampblack Cartridges with Different Wrappers*

Wrapper	Weight of Oxygen in Cartridge, Grams						Weight of Cartridge, Grams	Weight of Wrapper, Grams
	0 Min.	3 Min.	6 Min.	9 Min.	12 Min.	15 Min.		
Hard fiber cotton rag paper 0.007 in. thick, 1 thickness	173	139	112	86	64	45	31	3.0
Hard fiber cotton rag paper 0.007 in. thick, 2 thicknesses	171	139	113	88	65	47	34	5.0
Hard fiber cotton rag paper 0.007 in. thick, 3 thicknesses	176	143	117	92	71	53	37	7.0
Newsprint paper, 2 thicknesses	174	138	111	88	68	50	28	3.0
Wrapping paper, 0.006 in. thick, 2 thicknesses	171	136	105	79	58	43	37	8.0
Paper toweling, 2 thicknesses	172	140	112	85	65	45	34	5.0
Dynamite wrapper, not paraffined	165	133	105	79	56	40	35	7.5
Dynamite wrapper, paraffined	151	109	77	52	36	24	42	12.0

EXPLOSIVE PROPERTIES—THEORETICAL CONSIDERATIONS

The effect produced by an explosive in a bore hole depends on the energy and gas volume developed by unit weight of explosive, the loading density, and the rate at which the explosive reaction takes place. By making use of certain physical constants, it is possible to calculate the theoretical explosion temperature developed by an explosive, the energy density, and the maximum pressure produced—neglecting radiation and conduction. The method of calculation as applied to ordinary explosives requires some modification when used for L.O.X. Calculations are set forth in another paper by the writer[3] where it is shown that the experimental results given in the present paper may be predicted from theoretical considerations.

EXPLOSIVE TESTING METHODS[4]

The total energy of an explosive may be obtained by measuring in a calorimeter the heat evolved by the explosion. This represents the maximum capacity of the explosive for accomplishing work. In practice, however, the heated gases are cooled by radiation and conduction to the rock, and the actual work done is always a fraction of that which could theoretically be accomplished.

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[3] Future publication.

[4] Clarence Hall, W. O. Snelling, and S. P. Hall: Investigations of Explosives Used in Coal Mines. Bur. of Mines *Bull.* 15 (1912) 197.

When studying explosive properties, we distinguish between the propulsive or heaving effect and the disruptive or shattering effect. The magnitude of the propulsive effect depends on the total pressure produced by the explosive reaction, while the shattering effect depends on the speed at which the pressure is produced. No single piece of apparatus has been devised that will measure both the propulsive and disruptive effect. In the present work, the relative propulsive force of L.O.X. cartridges has been measured by the ballistic pendulum, and relative disruptive effect by measurement of the rate of detonation. Some determinations of the pressure produced have been made in the Bichel gage.

Volume Basis Used in Comparing Strength of L.O.X. Cartridges

In recording the results of strength tests of ordinary explosives, it is customary to use the weight basis as the standard of comparison. This is logical because such explosives are of unchanging composition, and for every pound purchased a pound may be charged into the bore hole. But with L.O.X., only about half of the oxygen produced in the plant is present in the saturated cartridges, because of losses in transportation, etc., and the cartridges begin to lose further quantities of oxygen immediately on removal from the liquid. Furthermore, the magnitude of these losses is a variable, depending on efficiency of containers, manipulation, and character of the cartridges, which change with local conditions.

It is misleading to use as the basis of comparison the weight of the L.O.X. cartridge at the moment of firing, because the loss in weight as oxygen evaporates is not necessarily accompanied by a proportionate loss in explosive strength. For example 1¼ by 8.6 in. cartridges, packed with lampblack, weighing 40 gm., volume 172 c. c., were fired at 5, 10, 15, and 20 min. after removal from the oxygen, and the unit deflective charge calculated on the basis of the weight of cartridge plus oxygen at time of firing; also the volume of cartridge necessary to give the same deflection (3.30 in.) as 227 gm. of the standard 40-per-cent. dynamite, as follows:

Time of Evaporation, Minutes	Weight of Cartridge Plus Oxygen, Grams	Deflection of Pendulum, Inches	Unit Deflective Charge	
			Grams	Cubic Centimeters
5	171	3.38	167	168
10	134	2.92	151	194
15	98	2.61	124	217
20	33	2.40	45	237

On the weight basis, the explosive is stronger with increase in time, but the decreasing swing of the pendulum shows that the cartridges become weaker as oxygen evaporates. Inasmuch as the weight of the cartridge at any time of firing bears no known relation to the cost, there seems no

good reason for using the weight basis of comparison. On the volume basis, the unit deflective charge at 5 min. is 168 c. c. and at 20 min., 237 c. c. The density of the standard dynamite is 1.32, and the volume of 227 gm. is 172 c. c., hence the L.O.X. cartridge has $\frac{172}{168} = 102$ per cent. the strength of 40-per-cent. dynamite if fired at 5 min., and $\frac{172}{237} = 73$ per cent. the strength of dynamite when fired at 20 min. The foregoing basis of comparison has been used in the present work with L.O.X. cartridges.

Tests of L.O.X. in Ballistic Pendulum

Table 6 shows the relative explosive strength, as determined by the ballistic pendulum, of lampblack cartridges of densities varying from

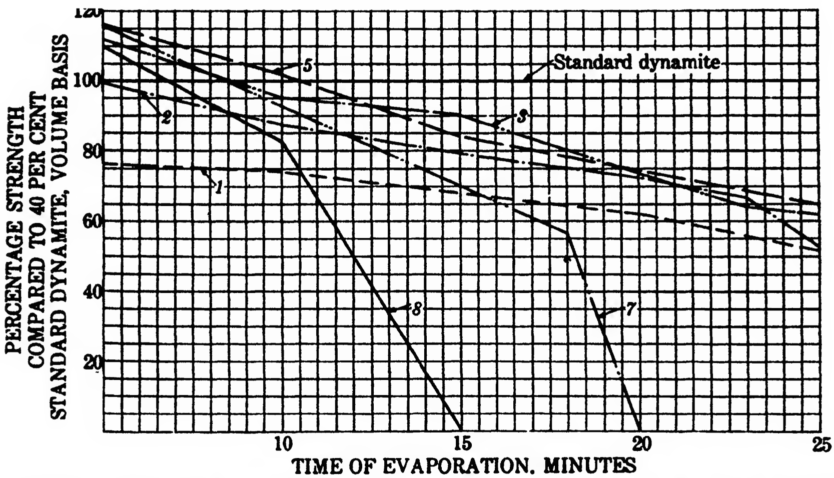


Fig. 8.—Relative strength as shown by ballistic pendulum of lampblack and gas-black cartridges of various densities. 1, lampblack E, 0 175 gm per c. c.; 2, lampblack E, 0.23 gm. per c. c.; 3, gas black ES, 0.29 gm. per c c.; 5, gas black S, 0.38 gm. per c. c.; 7, gas black TS, 0.49 gm. per c. c.; 8, gas black T, 0.58 gm. per c. c.

0.17 to 0.58 gm. per c. c. at times of evaporation varying from 5 to 25 min. Similar data are given for a number of other combustible mixtures; the data are plotted in Figs. 8 to 12. The cartridge wrappers, weight 5 gm., were made of two thicknesses of absorbent hard fiber cotton rag paper and were 1¼ in. outside diameter by 8.6 in. long, having the same volume as 227 gm. of the standard dynamite. Because of a number of variables, the deflection of the pendulum produced by the standard dynamite varies slightly from day to day. For comparative purposes, the deflections given in Table 6 have been corrected to correspond to a standard deflection of 3.30 in. for 227 gm. of dynamite. The deflection of the pendulum has been taken as proportional to the weight of the charge, an assumption not strictly true, but sufficiently accurate considering other experimental errors.

TABLE 6.—*Propulsive Strength of L.O.X. Cartridges as Measured by Ballistic Pendulum*

	Cartridge Weight		Oxygen per Gram of Cartridge			Life, Minutes	Time of Evaporation, Minutes	Deflection		Weight of Dry Cartridge Equal to 227 Grams of Dynamite Grams	Unit Deflective Charge, Cubic Centimeters	Relative Strength by Volume Compared to Dynamite
	Dry, Grams	Soaked, Grams	Absorbed Initially	Required for Complete Combustion	At Time of Firing			Per Cartridge, Inches	Per Gram, Inches			
1. Lampblack E, cartridge density 0.175.	33	215	5.52	2.21	4.10	13	5	2.76	0.084	39.5	206	0.84
	30	216	6.20	2.20	3.40	15	10	2.43	0.081	40.7	234	0.74
	31	214	5.90	2.20	2.06	14.5	15	2.35	0.076	43.6	242	0.71
	31	216	5.97	2.20	1.35	14.5	20	2.10	0.068	48.7	270	0.64
	29	215	6.40	2.17	0.97	16	25	1.64	0.057	58.4	346	0.50
2. Lampblack E, cartridge density 0.23.	38	225	4.92	2.24	3.50	12	5	3.13	0.082	40.1	181	0.95
	39	222	4.70	2.24	2.44	11.5	10	2.86	0.073	45.0	199	0.87
	40	230	4.75	2.24	1.45	11	15	2.61	0.065	50.6	218	0.79
	40	223	4.57	2.24	0.83	11	20	2.40	0.060	55.0	237	0.73
	38	225	4.93	2.24	0.58	12	25	1.68	0.044	74.6	338	0.51
3. Gas black ES, cartridge density 0.29.	51	224	3.40	2.32	2.38	5	5	3.75	0.074	44.9	151	1.14
	47	220	3.68	2.31	1.70	7	10	2.95	0.063	52.6	192	0.89
	48	223	3.64	2.31	1.27	7	15	2.86	0.060	55.4	199	0.87
	48	223	3.64	2.31	0.52	7	25	1.95	0.041	81.2	291	0.59
4. Lampblack D, cartridge density 0 33.	57	230	3.04	2.46	2.30	4	5	3.76	0.066	50.0	151	1.14
	57	226	2.96	2.46	1.88	4	8	3.37	0.059	55.8	169	1.02
	59	220	2.73	2.46	1.55	4	10	3.23	0.055	60.3	176	0.98
	57	225	2.94	2.46	0.98	4	15	2.42	0.042	77.8	235	0.73
	58	225	2.88	2.46	0.59	4	18	1.83	0.032	104.6	310	0.55
	57	225	2.94	2.46	0.53	4	20	0.50	0.009	376	1135	0.15
5. Gas black S, cartridge density 0.38.	65	225	2.46	2.43	1.78	0.5	5	3.84	0.059	55.8	148	1.16
	65	228	2.50	2.43	1.48	0.5	8	3.45	0.053	62.2	165	1.05
	64	228	2.56	2.43	1.28	1.0	10	3.31	0.052	63.8	172	1.00
	64	225	2.52	2.43	0.92	1.0	15	2.75	0.043	76.8	206	0.83
	64	235	2.67	2.43	0.77	1.0	18	2.65	0.041	79.8	214	0.80
	64	232	2.62	2.43	0.56	1.0	23	2.37	0.037	89.2	240	0.72
	64	232	2.62	2.43	0.50	1.0	25	2.13	0.033	99.2	266	0.65
6. Gas black TS, cartridge density 0.43.	74	235	2.18	2.47	1.48	0	5	3.75	0.051	65.2	151	1.14
	73	237	2.24	2.47	0.99		10	3.15	0.043	76.5	180	0.95
	74	235	2.18	2.47	0.65		15	2.67	0.036	91.4	213	0.81
	76	236	2.10	2.48	0.51		18	2.39	0.031	105	238	0.72
	73	235	2.22	2.47	0.42		23	1.88	0.026	128	302	0.57

7. Gas black TS, cartridge density 0.49.	83	237	1.85	2.51	1.19	0	5	3.77	0.045	72.6	151	1.14
	85	240	1.82	2.51	0.71		10	3.09	0.036	90.7	184	0.94
	84	235	1.80	2.51	0.45		15	2.30	0.027	120.5	247	0.70
	84	235	1.80	2.51	0.37		18	1.87	0.022	148	308	0.57
8. Gas black T, cartridge density 0.58.	100	245	1.45	2.54	0.95	0	5	3.62	0.036	91.2	157	1.10
	100	235	1.35	2.54	0.51		10	2.65	0.027	124.5	214	0.80
	100	240	1.40	2.54	0.21		15	0.0	0.000	∞	∞	0.00
9.[a] ½ gas black S, ½ kieselguhr......	60	233	5.32	2.32	2.62	12	10	2.40	0.074	44.7	237	0.73
	62	225	5.15	2.32	1.58		15	2.25	0.067	49.1	252	0.68
	62	235	5.16	2.32	0.84		20	1.75	0.052	63.2	324	0.53
10. 60% kieselguhr, 40% fuel oil......	83	223	1.69	1.34	1.28	2.5	3.2	3.15	0.038	87.0	180	0.96
	83	223	1.69	1.34	1.08	2.0	5	3.00	0.036	91.3	189	0.90
	84	220	1.62	1.34	0.54	2.0	10	2.34	0.028	118.0	243	0.71
	80	220	1.75	1.34	0.25	3.0	15	1.50	0.019	105.6	378	0.46
11. 15% oil, 85% wood pulp..........	63	210	2.34	1.60	1.23	3	5	3.05	0.049	68.2	186	0.92
	65	215	2.31	1.61	0.49	3	10	2.30	0.035	93.3	247	0.70
	66	215	2.26	1.61	0.15	3	15	1.20	0.018	181.5	473	0.36
12. 20% lampblack, 80% wood pulp...	61	216	2.54	1.55	1.66	5	5	3.19	0.052	63.1	178	0.97
	61	220	2.60	1.55	0.77	5	10	2.88	0.047	69.9	197	0.87
	64	228	2.47	1.55	0.25	5	15	2.05	0.032	103.1	277	0.62
13. 55% coal dust, 45% kieselguhr....	84	232	1.76	1.28	1.12	4	5	3.13	0.037	88.6	181	0.95
	84	230	1.74	1.28	0.61	4	10	1.10	0.013	252.0	516	0.33
14. 78% peat, 22% kieselguhr........	100	230	1.30	1.18	1.05	1.5	3	3.54	0.035	93.2	160	1.07
	103	230	1.23	1.19	0.60	0.5	8	2.65	0.026	128.3	214	0.80
	100	230	1.30	1.18	0.40	1.5	12	1.05	0.011	314.3	540	0.32
15. Carbene........................	47	210	3.47	2.73	2.28	3	5	3.74	0.080	41.5	152	1.13
	46	207	3.50	2.73	1.39	3	10	3.13	0.068	48.5	181	0.95
	46	207	3.50	2.73	0.63	3	20	1.38	0.030	110.0	414	0.42
80% gas black ES, 20% FeSi..........	61	215	2.53	2.08	1.69	5	9	3.11	0.051	64.7	183	0.94
80% gas black ES, 20% aluminum....	56	220	2.93	2.11	1.27	5	9	3.08	0.055	60.0	184	0.93
50% gas black ES, 30% naphthalene, 20% kieselguhr....................	70	216	2.08	2.06	1.56	5	9	3.08	0.044	75.0	184	0.93
91% aluminum, 9% kieselguhr........	126	285	1.26	0.75	0.69	7	8	3.08	0.024	135	184	0.93
72.6% aluminum, 27.4% kieselguhr....	100	260	1.60	0.67	0.88	10	8	2.50	0.025	132	227	0.76
Cartridge paper....................	58	210	2.62	1.08	1.02	5.5	6	2.60	0.045	73.6	218	0.79
Stic of yellow pine................	76	196	1.58	1.40	1.22	1.5	3	3.43	0.045	73.1	165	1.04
60% $MgCO_3$, 40% fuel oil............	82	218	1.66	1.34	1.21	3	4	3.28	0.040	82.5	173	0.99
	82	220	1.68	1.34	0.60	3	10	2.38	0.029	113.6	238	0.72

[a] Ratios are per gram of combustible, *i. e.*, black plus wrapper.

Table 7 shows comparative strength of two series of cartridges packed to such density that, at a given time, the oxygen ratio is 2.4 and 1.5, respectively.

Conclusions

Conclusions to be drawn from Tables 6 and 7 and Figs. 6 to 10 are as follows:

1. For lampblack cartridges 1¼ in. in diameter, the optimum packing density, for general use, is about 0.30 gm. per c. c. These cartridges have a life, for evaporation to conditions of complete combustion, of 5 min. and, at this time, a propulsive strength per unit volume 15 per cent. greater than the standard dynamite; after 25 min. evaporation the strength is still 65 per cent. that of dynamite.

2. If the presence of carbon monoxide in the products of the explosion is undesirable, lighter packing densities must be used for loading operations taking longer than 5 min., see Table 7. For example, a cartridge weighing 0.27 gm. per c. c. will have sufficient oxygen for complete combustion after 8 min. evaporation and propulsive strength per unit volume 97 per cent. that of dynamite; a cartridge weighing 0.23 gm. per c. c. may be fired at 10 min. with a strength 87 per cent. that of dynamite; and a cartridge weighing 0.175 gm. per c. c. may be fired in 14 min. with a strength 70 per cent. that of dynamite.

3. As the cartridges lose weight through evaporation of oxygen, the propulsive strength does not show a proportional decrease. For cartridges of a given weight, the difference in strength between a cartridge fired when the ratio of oxygen to carbon is 2.4 and a cartridge fired when this ratio is 1.3, is only 15 to 20 per cent.

4. Due to the low latent heat of vaporization of liquid oxygen, excess oxygen over that required for complete combustion gives increased strength. For example, a cartridge fired when the oxygen-carbon ratio was 3.5, was 12 per cent. stronger per unit weight than a similar cartridge fired when the ratio was 2.4.

5. The strength per unit weight, for a given oxygen-cartridge ratio, decreases with increasing density, as shown in Fig. 9. For example, a cartridge of lampblack E, density 0.23 gm. per c. c., fired when the oxygen ratio was 1.45, gave a deflection of 0.065 in. per gm. of cartridge; while a cartridge of gas black S, density 0.38 gm. per c. c., fired when the ratio was 1.48, gave but 0.053 in. per gm. of cartridge. That the decrease in explosive effect per gram of material is not due to any peculiarity of the different lampblacks other than density, is shown by results with cartridge 9, which was composed of 50 per cent. gas black S and 50 per cent. of the inert material, kieselguhr. The deflection per gram of combustible was 0.65 in. when the weight ratio of oxygen to cartridge was 1.48, as against 0.53 in. for the undiluted black, showing that the effect is connected with

TABLE 7.—*Relative Strength of Cartridges of Such Density That at Given Time of Evaporation Oxygen Ratio is 2.4 and 1.5*

Time of Evaporation, Minutes	Cartridge Density When Oxygen Ratio is		Per Cent. Propulsive Strength[a] When Oxygen Ratio is	
	2.4	1.5	2.4	1.5
5	0.29	0.435	112	116
8	0.27	0.38	97	108
10	0.23	0.335	87	100
12	0.20	0.29	77	93
14	0.175	0.25	70	85

[a] As measured by ballistic pendulum, compared with 40 per cent. standard dynamite, volume basis.

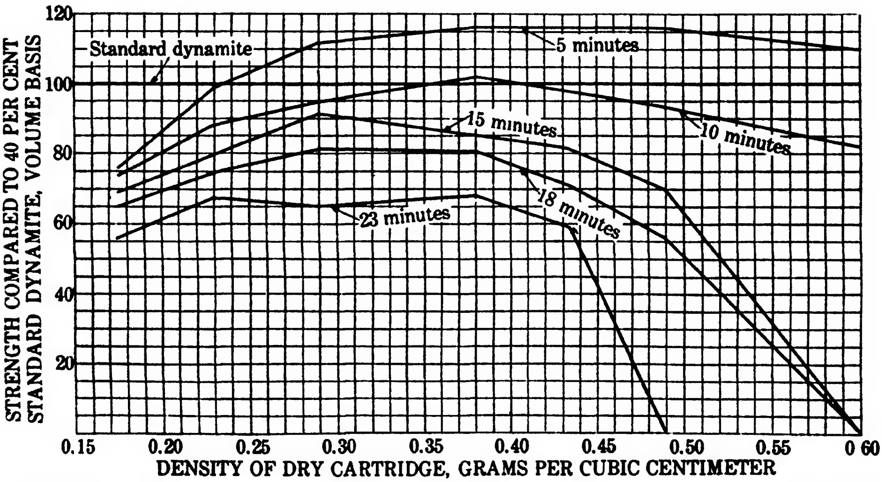


FIG. 9.—RELATIVE STRENGTH OF LAMPBLACK AND GAS-BLACK CARTRIDGES PLOTTED AGAINST DENSITY.

the density of the combustible material. As radiation from a gas is proportional to the square root of the density, it seems probable that the percentage loss by radiation is greater in the case of the heavier cartridges, because of the greater gas density produced.

6. While carbene is initially about 8 per cent. stronger on a weight basis than lampblack, this material shows a disadvantage over lampblack because of the more rapid loss in strength as a result of the higher rate of evaporation of oxygen from this material.

7. Oil-kieselguhr mixtures have fairly good initial strength, but lose strength rapidly as time of evaporation increases. For example, a mixture of 40 per cent. fuel oil with 60 per cent. kieselguhr had a strength 90 per cent. that of dynamite at 5 min., but by 15 min. had fallen to 45 per cent.

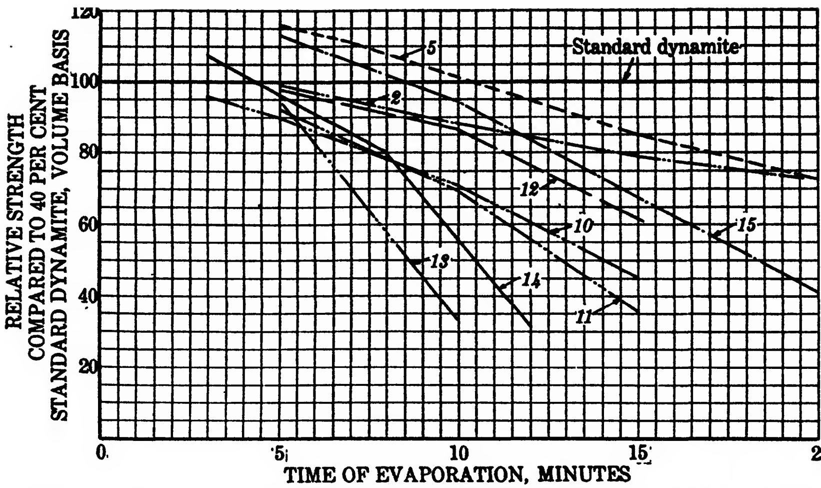


FIG. 10.—EXPLOSIVE STRENGTH OF VARIOUS MIXTURES AT DIFFERENT TIMES OF EVAPORATION, AS SHOWN BY BALLISTIC PENDULUM; 2, LAMPBLACK, 0.23 GM. PER C. C.; 5, GAS BLACK, 0.38 GM. PER C. C.; 10, 40 PER CENT. FUEL OIL, 60 PER CENT. KIESELGUHR; 11, 15 PER CENT. FUEL OIL, 85 PER CENT. WOOD PULP; 12, 20 PER CENT. LAMPBLACK, 80 PER CENT. WOOD PULP; 13, 55 PER CENT. COAL DUST, 45 PER CENT. KIESELGUHR; 14, 78 PER CENT. PEAT, 22 PER CENT. KIESELGUHR; 15, CARBENE.

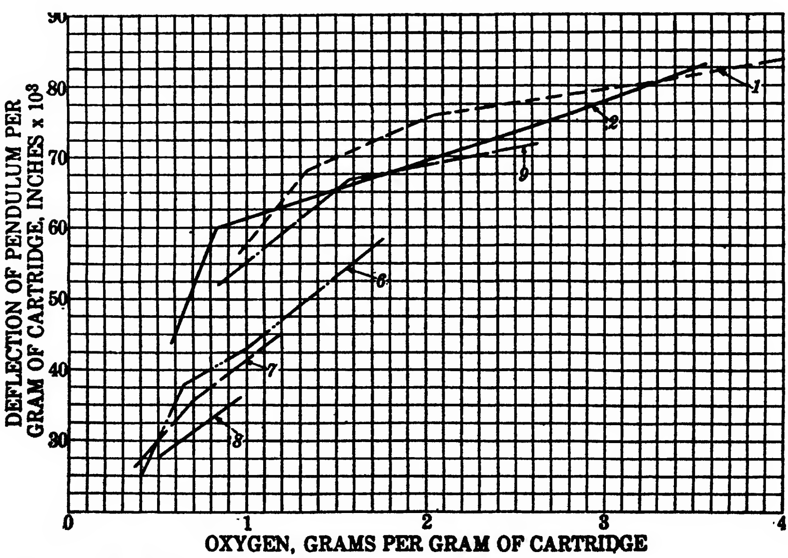


FIG. 11.—RELATION BETWEEN OXYGEN CONTENT PER GRAM OF CARTRIDGE AT TIME OF FIRING AND EXPLOSIVE STRENGTH PER GRAM AS MEASURED BY THE BALLISTIC PENDULUM; 1, LAMPBLACK E, 0.175 GM. PER C. C.; 2, LAMPBLACK E, 0.23 GM. PER C. C.; 6, GAS BLACK TS, 0.435 GM. PER C. C.; 7, GAS BLACK TS, 0.49 GM. PER C. C.; 8, GAS BLACK T, 0.58 GM. PER C. C.; 9, 50 PER CENT. GAS BLACK S, 50 PER CENT. KIESELGUHR.

8. Other mixtures containing no lampblack, such as oil-wood pulp, coal dust-kieselguhr, peat-kieselguhr, show good initial strength, but because of rapid loss of oxygen by evaporation they lose their effectiveness more rapidly than the lampblack.

9. Admixture of 20 per cent. lampblack with wood pulp increases its retentivity of oxygen so that, for periods of firing up to 10 min., it shows the same strength as a lampblack cartridge of density 0.23.

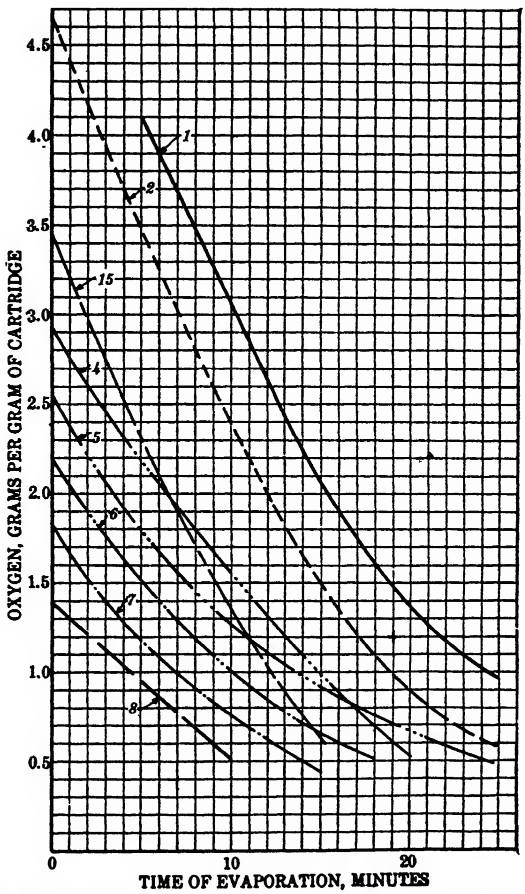


FIG. 12.—RATE OF EVAPORATION IN BALLISTIC CANNON.

10. Admixture of aluminum or ferrosilicon to lampblack does not materially affect the explosive strength.

11. A cartridge packed with a mixture of 91 per cent. powdered aluminum and 9 per cent. kieselguhr showed a strength, after 8 min. evaporation, about equal to a lampblack cartridge of density 0.23. The gases produced by the cartridge paper are sufficient to account for only a fraction of the explosive strength if the combustion of aluminum is assumed

to produce no gas. The boiling point of aluminum oxide is 2210° C and gaseous aluminum oxide is undoubtedly present at the instant of explosion; see also Table 9.

12. Comparison of these data with Table 3 shows the desirability of cartridges of as large diameter as feasible. For example, with 2-in. cartridges the time figures given in Tables 6 and 7 would be doubled. For quarry work, where 5-in. cartridges may be used, a large variety of cheap materials are available on account of the greatly increased life of these cartridges.

Gases Evolved and Pressure Produced as Determined in Bichel Gage

A number of experiments have been carried out in the Bichel gage to determine products of combustion of L.O.X. cartridges fired after different periods of evaporation. In the procedure employed with ordinary

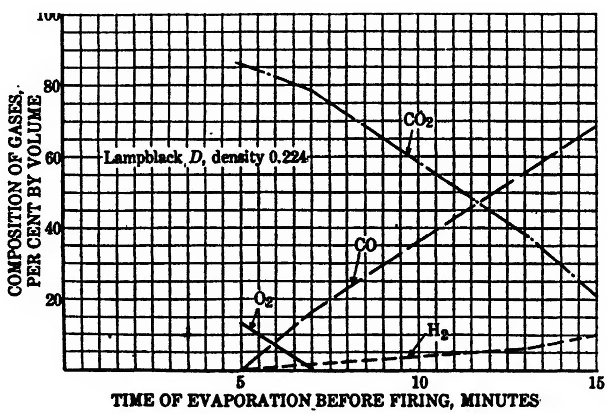


Fig. 13.—Composition of gaseous products of explosion as measured in Bichel gage; lampblack D, density 0.224 gm. per c. c.

explosives, the gage is evacuated before firing. As this is impossible with L.O.X., in conducting these tests the cartridge is allowed to evaporate in the gage with the vent valve open until the instant before firing. By this procedure, the cartridge is fired in an atmosphere of nearly pure oxygen, which also takes part in the explosive reaction. Results obtained with the Bichel gage are interesting, but give little additional information over that obtained by an evaporation test and a measurement of propulsive strength in the ballistic cannon. The amount of carbon monoxide to be expected can be predicted fairly well from evaporation test data, and the pressures as measured by the gage agree fairly well with results of the ballistic pendulum tests. Table 8 and Figs. 13 and 14 give data

obtained by firing cartridges packed with lampblack D and gas black S after different evaporation periods. Table 9 gives data obtained with cartridges 1½ by 6 in. (weight of wrapper 5 gm.) packed with various combustible mixtures, and shows volume of gases produced, gas composition, and maximum pressure produced as measured by the recording gage. Table 10 gives data obtained with gas black S, as determined with three cooling surfaces, in order to calculate the pressure that the explosive should theoretically develop if detonated when confined in its own volume.

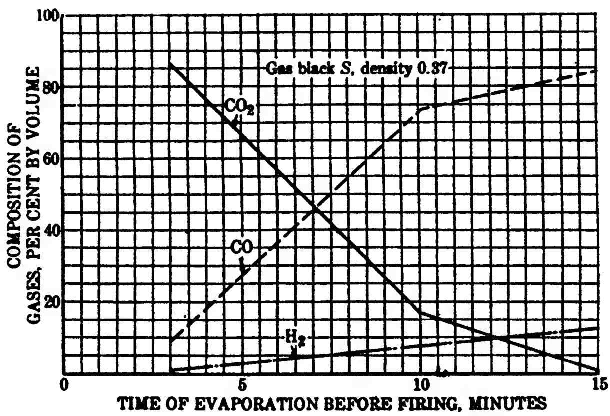


FIG. 14.—COMPOSITION OF GASEOUS PRODUCTS OF EXPLOSION AS MEASURED IN BICHEL GAGE; GAS BLACK S, DENSITY 0.37 GM. PER C. C.

TABLE 8.—*Products of Combustion after Different Evaporation Periods*

Time of Evaporation, Minutes	Weight of Cartridge, Grams	O_2 per Gram for Complete Combustion	O_2 in Cartridge when Fired, Grams per Gram	Volume of Gases at 0° and 760 Mm., Liters	Composition of Gases					
					CO_2, Per Cent.	O_2, Per Cent.	CO, Per Cent.	H_2, Per Cent.	CH_4, Per Cent.	N_2, Per Cent.
Lampblack D, 1¼ by 12 in. cartridges										
5	52	2.34	2.7	100.7	85.6	12.7	0.3	0.0	0.0	1.4
7	53	2.34	2.3	97.3	79.3	0.0	16.5	2.1	0.3	1.8
13	52	2.34	1.7	92.5	38.3	0.0	54.7	6.1	0.0	0.9
15	52	2.34	1.2	79.1	21.0	0.0	68.4	9.6	0.0	1.0
Gas black S, 1¼ by 8 in. cartridges										
3	60	2.40	2.10	108	87.0	0.0	9.2	0.8	0.0	3.0
10	60	2.40	1.15	108	18.3	0.0	73.2	0.0	0.0	0.8
15	58	2.40	0.80	105	0.9	0.0	84.0	12.5	0.0	2.6

TABLE 9.—*Tests of L.O.X. Cartridges in Bichel Gage*

Cartridge Composition	Weight of Cartridge		Oxygen in Cartridge When Fired, Grams per Gram	Time of Evaporation, Minutes	Volume of Gases at 0° and 760 Mm., Liters	Analysis of Gaseous Products						Normal Pressure, Kg. per Sq. Cm. 1¼ by 6 In. Cartridge	Normal Pressure, Kg. per Sq. Cm. 1¼ by 8 In. Cartridge
	Dry	Soaked				CO_2, Per Cent.	O_2, Per Cent.	CO, Per Cent.	H_2, Per Cent.	CH_4, Per Cent.	N_2, Per Cent.		
Gas black S	52	214	93	10	92.8	66.3	0.0	28.2	4.0	0.4	1.1	103.4	95.7
	52	214	72	14	94.9	34.8	0.0	56.1	7.5	0.3	1.3	85.9	79.6
Wood pulp	61	215	98	5	66.9	84.2	13.0	0.4	0.1	0.0	2.3	99.2	91.9
Carbene	42	210	63	14	76.2	43.5	0.0	45.3	9.7	0.2	1.3	82.0	76.0
50 % gas black, 30 % naphthalene, 20 % kieselguhr	70	220	63	14	118.0	6.0	0.0	72.7	19.5	0.5	1.3	75.0	69.4
80 % gas black, 20 % aluminum	57	215	72	14	87.8	35.3	0.0	54.6	8.5	0.3	1.3	85.9	79.6
80 % gas black, 20 % ferrosilicon	60	220	75	14	94.5	21.9	0.0	73.7	3.9	0.5		84.4	78.1
85 % aluminum,[a] 15 % kieselguhr	115	247	80	6	17.6	43.5	0.04	28.0	19.3	0.13	9.03		64.1

[a] 1¼ by 8 in. cartridge.

Rate of Detonation of L.O.X. Cartridges

Results obtained with the ballistic pendulum represent the heaving effect of an explosive. In determining the efficacy of an explosive, the velocity of propagation of the explosion wave must be considered as this determines the speed at which the energy is liberated. The more rapid the rate of detonation, the greater will be the shattering effect of the explosive.

Table 10.—*Determination of Pressure Developed in Own Volume*

Gas black S, time of evaporation 10 min., weight of dope and wrapper 52 gm., weight of O_2 present at time of firing 93 gm., total weight of charge, 145 gm.

Cooling Area, Square Centimeters	Height of Curve, Millimeters	Pressure, Kilograms per Square Centimeter	Average Pressure, Kilograms per Square Centimeter
A 3914	32.25	100.78	
3914	33.50	104.69	
3914	33.50	104.69	103.39
B 6555	28.00	87.50	
6555	30.50	95.31	91.40
C 7624	29.50	92.19	
7624	30.00	93.75	92.97

$$
\begin{aligned}
P &= 1.911A + 0.5B - 1.411C \\
&= (1.911 \times 103.39) + (0.5 \times 91.40) - (1.411 \times 92.97). \\
&= 112.1 \text{ kg. per sq. cm.}
\end{aligned}
$$

Let pressure in its own volume be M

$$M \quad \frac{VPS}{W} \quad 9625 \text{ kg. per sq. cm.}$$

where $W = 145$ gm. and $S = 0.83$ gm. per sq. cm.

Rates of detonation of L.O.X. cartridge have been determined by the Dautriche method. Table 11 shows rates for a number of cartridge compositions; Table 12 shows rates of detonation of a lampblack cartridge at different evaporation periods before firing.

Conclusions

Conclusions to be drawn from the data in Table 11 are as follows:

1. The rate of detonation of gas-black cartridges varies from 4900 to 6200 m. per sec., increasing with the density.

2. The rate of detonation of lampblack cartridges varies from 4200 to 5000 m. per sec., increasing with the density.

3. Loosely packed lampblack cartridges detonate erratically, giving rates varying from 1000 to 5000 m. per sec.

4. Mixtures of oil and kieselguhr detonate at around 3200 m. per sec.; mixtures of oil and magnesium carbonate, containing up to 40 per cent. oil detonate around 4000 m. per sec.; while higher percentages of oil detonate around 3200 m. per sec.

TABLE 11.—*Rate of Detonation of L.O.X. Cartridges*

Material	Weight, Grams	Time of Evaporation, Minutes	Rate of Detonation, Meters per Second
Lampblack M	34	8	1000–5275 (loosely packed)
Lampblack M	42	6	5100
Lampblack B	50	5	800–4000
Lampblack C	49	5	5100
Lampblack E	30	10	4200
Lampblack D	52	5	5000
Gas black K	45	7	4900
Gas black A	55	4	5300
Gas black S	50	6	5000
Gas black S	60	3	6200
Acetylene black	42	8	4350
29 % fuel oil, 71 % kieselguhr	70	5	3100
35.5 % fuel oil, 64.5 % kieselguhr	75	5	3150
40 % fuel oil, 60 % kieselguhr	78	3	3200
28.6 % fuel oil, 71.4 % $MgCO_3$	65	8	3600
40 % fuel oil, 60 % $MgCO_3$	75	4	4000
50 % fuel oil, 50 % $MgCO_3$	85	2	3200
60 % fuel oil, 40 % $MgCO_3$	110	2	3200
15 % fuel oil, 85 % wood pulp	58	3	4250
20 % lampblack D, 80 % wood pulp	55	3	4800
20 % kieselguhr, 80 % lampblack D	55	3	4510
55 % coal dust, 45 % kieselguhr	78	3	Misfire
20 % aluminum, 80 % lampblack D	55	5	4800
Carbene	42	5	5200
50 % coal dust, 45 % kieselguhr, 5 % carbene	75	5	1000–3500

TABLE 12.—*Effect of Evaporation Time on Rate of Detonation*

Lampblack D, 1½ by 8 in. cartridges, weight 68 gm.

Time, Minutes	O_2 per Gram, Grams	Rate of Detonation, Meters per Second
4	2.68	5350
6	2.40	5220
9	1.78	5250
12	1.69	5090
22	0.85	5270
27	0.68	4860
30	0.56	4670

5. The rate of detonation is determined by the constituent present in the finest state of subdivision; for example; a mixture of 20 per cent. lampblack and 80 per cent. wood pulp detonates at 4800 m. per sec., or nearly the same as lampblack alone.

6. Mixtures containing coarse non-absorbent particles, such as coal dust, detonate at low rates and erratically, from 1000 to 3500 m. per.sec.

7. Addition of aluminum to lampblack does not affect the rate of detonation appreciably.

8. Addition of 20 per cent. kieselguhr lowers the rate about 500 m. per sec.

9. Lampblack cartridges detonate at practically the same rate, whatever the time of evaporation before firing.

Explosion by Influence Tests

When an explosive is charged into a bore hole, all the cartridges may not be in contact with one another, but may be separated at some point by an air gap. The explosion by influence test is designed to show the air gap between cartridges over which the explosion wave may be transmitted.

In the tests with L.O.X., the test has been conducted by rolling two cartridges in two thicknesses of wrapping paper with the desired gap between the cartridges and detonating one of the cartridges. The test is conducted with successively increasing distances between cartridges, until no detonation of the second cartridge is obtained. The maximum distance over which the explosion will always be propagated is shown in Table 13.

Table 13.—*Sensitivity to Explosion by Influence*

Material	Weight of Cartridge, Grams	Weight of O_2, Grams	Firing Time, Minutes	Maximum Distance of Explosion, Inches
Lampblack D	50	210	4	6
Acetylene black	41	211	4	6
Carbon black S	63	223	3	30
Lampblack E	40	220	6	20
Carbene	40	200	3	20+
18.4 % naphthalene, 81.6 % lampblack D	52	210	3	20
14.3 % carbene, 85.7 lampblack D	54	212	4	20
15 % gilsonite, 85 % lampblack D	55	210	4	20
40 % fuel oil, 60 % kieselguhr	75	205	4	12

The tests show that lampblacks containing but a small amount of volatile matter are rather insensitive to explosion by influence, the gap jumped being 6 in. In the case of lampblack, such as E, containing more volatile matter, the gap increases to 20 in. Cartridges of the dense gas

black S jump a gap of 30 in. Carbene cartridges are sensitive over at least 20 in.; insufficient material was available to make further tests of this material. The addition of naphthalene, carbene, or gilsonite to an insensitive lampblack, such as D, increase the gap jumped to 20 in. The kieselguhr-oil mixtures jump a gap of 12 in. Hydrocarbons evidently tend to make the mixture more sensitive to explosion by influence.

Sensitivity of L.O.X. to Explosion by Impact

A few experiments have been made to determine the sensitivity of various L.O.X. mixtures to explosion by impact, using the large impact device[5] at the Bureau testing station. Gas black and carbene require a drop of 20 cm. for explosion and a gas black-ferrosilicon mixture, 2.5 cm. Commercial dynamites require a drop of 5 to 10 cm.

Detonation of L.O.X. with Fuse Alone

Liquid-oxygen cartridges burn without detonation when unconfined. When confined in the bore hole, the lampblack and gas-black cartridges sometimes burn without explosion but very frequently detonate. Cartridges containing hydrocarbons, such as petroleum oil, gilsonite, or carbene, always detonate if ignited under confinement. There is reason to believe, however, that the rate of detonation is considerably less than when these cartridges are detonated by a fulminate cap or other detonating agent. In Germany, when a brisant effect is not desired, no detonator is employed. Experiments are in progress to determine the feasibility of blasting with certain mixtures without the use of a detonator.

The present investigation has endeavored to determine the factors governing the explosive properties of typical combustible materials used in L.O.X. in the hope that such fundamental data will be of assistance in developing cartridges suitable for various blasting operations. Further work is in progress in which different cartridge compositions are being tested in actual blasting.

Acknowledgments

The writer acknowledges his appreciation of the advice and assistance rendered by Mr. J. E. Crawshaw, engineer in charge of explosives testing, and extends his thanks to Messrs. A. B. Coates, D. B. Gawthrop, and E. Stein, engineers in the explosives section, who assisted in part of the experimental work. Mr. Geo. B. Holderer, engineer with the Air Reduction Co., gave valuable suggestions during the course of the investigation. The work was carried out under the general supervision of A. C. Fieldner, supervising chemist, Pittsburgh Experiment Station, Bureau of Mines.

[5] Clarence Hall and S. P. Howell: Tests of Permissible Explosives. Bur. of Mines *Bull.* 66, (1913) 17.

DISCUSSION

George S. Rice,* Washington, D. C.—It is well to state to a meeting of coal-mining men that the Bureau of Mines does not advocate the use of liquid-oxygen explosive in coal mines, for while the flame is short, it is of long duration and there is no reasonable hope of making this a permissible explosive for use in coal mines. During the war, when there was a shortage of nitrate (practically at the beginning of the war), we saw a notice in the German papers that they were starting to use these explosives and the Bureau at once began its investigations of the subject. The explosive is being used to advantage by a few companies in South America and I understand it is being used at a quarry in Pennsylvania. The Bureau was obliged to put aside its investigation of "L.O.X." for awhile but renewed it a little over a year ago.

This explosive is composed primarily of oxygen and carbonaceous material. The carbonaceous material may be a great variety of things. It is so easy to make an explosive in that way that liquid oxygen has been somewhat misjudged from the start. After seeing it used during the Armistice period in the Lorraine iron mines, where it had been extensively used, I felt that it was a good deal easier to use than it later proved to be. They fired one shot at a time and thereby made its use comparatively easy. It worked very well there. Something like 60 per cent. of the Lorraine iron ore is mined by its use.

When liquid oxygen was used in rounds of shots in underground work, there was increasing danger. Also, the tendency is for the one-man drill. With the decrease in the dimension of cartridges, there is an increase in the rate of evaporation. The cartridge must be fired within a certain period. In the first stage there is excess of liquid oxygen and practically no poisonous fumes result, but only CO_2 is produced; but after five or ten minutes have passed, on discharge carbon monoxide is formed in increasing quantities. The explosive has the virtue that there are no misfires to dig out.

In quarrying, it has a great field, which has not been fully developed. I saw it used last year in blasting down 6000 tons of rock in a quarry; the previous summer in France I had seen it used at a limestone quarry to bring down 10,000 tons of rock. When used that way with the large cartridges, the evaporation is much slower; I think that one of the largest fields will be in that direction. During the war Germany used it in all except the most gaseous mines; it was the universal commercial explosive. The military authorities wanted the nitrate for military ammunition.

* Chief Mining Engineer, Bureau of Mines.

Increasing Production of Petroleum by Increasing Diameter of Wells

By Lester C. Uren,* Berkeley, Calif.

(New York Meeting, February, 1925)

Petroleum occurs, in nature, as a fluid saturating the pore spaces between the grains of porous rocks or aggregations of rock particles such as sand, sandstone, conglomerate, shale, limestone, etc. The oil, under the influence of gas pressure, hydrostatic pressure, gravity, earth pressure, and, perhaps, other natural forces, is caused to flow through the porous "reservoir rock" into wells penetrating the stratum in which the oil occurs. The principal moving force is the pressure of dissolved or occluded natural gas within the oil, though this force is assisted by gravity and by the hydrostatic or buoyant pressure of ground water about the edges of the "pool." The wells, providing outlets to the surface, are centers of reduced pressure and the flow of rock fluids into a particular well is usually an expression of the difference in pressure existing between the space within the well and that of the stored oil within the reservoir rock. The greater this differential pressure, the more rapidly will oil flow from the source rock into the well. Opposing movement of the oil from the reservoir rock into the well are certain natural forces related to the rock structure, such as pore friction and capillarity, and certain others related to the physical properties of the oil, such as viscosity and adhesion. The differential pressure between the well and the boundaries of the area drained by it must be sufficient to overcome the forces opposing flow if there is to be movement of oil into the well. If by any device the resistance to movement of the oil may be reduced, the oil will flow into the well at a more rapid rate and the effective area of drainage will be increased.

* Associate Professor of Petroleum Engineering, University of California.

Relation of Variables Governing Flow of Liquids through Sands

It has been shown by King[1] that both water and oil flowing at low velocities through sands follow, in a general way, the laws of viscous flow, a condition which in the case of flow through a cylindrical tube, is expressed by the formula of Poiseuille:

$$P = \frac{0.000668\, Z\, L\, V}{D^2 S}, \tag{1}$$

in which P = pressure drop, in pounds per square inch; Z = absolute viscosity of oil in centipoises; L = length of tube, in feet; V = average linear velocity of flow, in feet per second; S = specific gravity of fluid; and D = inside diameter of tube, in inches.

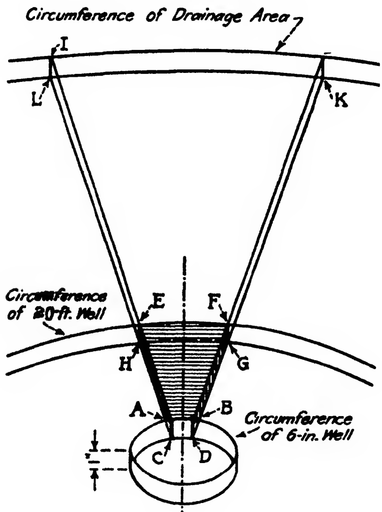


Fig. 1.

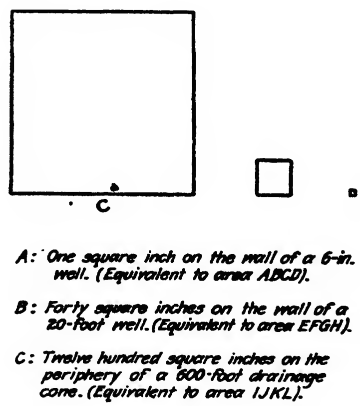


Fig. 2.

Fig. 1.—Horizontal, wedge-shaped segment of drainage area of a well, showing increase in cross-sectional area available for oil flow resulting from increase in diameter of well.

Fig. 2.—Relative cross-sections of drainage wedge 3 in., 10 ft., and 300 ft., from axis of well.

According to this formula, the pressure loss varies directly with the velocity and inversely with the area of cross-section through which flow occurs; that is, doubling the effective pressure doubles the rate of flow, or, assuming that the velocity remains constant, doubling the cross-sectional flow area reduces the pressure loss one-half.

[1] F. H. King: Principles and Conditions of Movements of Ground Water. U. S. Geol. Sur. 19th. *Ann. Rept.*, part 2 (1897–98).

A horizontal, wedge-shaped segment of drainage area of a well is shown in Fig. 1. If it is assumed that the well is 6 in. in diameter and that it is effective in drawing oil from a circular area 600 ft. in diameter with the well as a center, by substitution in the formula, it will be found that a large part of the energy latent within the oil is expended in moving it through the sand within 10 ft. of the well. This is because of the great constriction in cross-sectional area of the segment as the well is approached. Thus, in Fig. 1, if the area *ABCD* cut by the segment on the wall of the 6-in. well is 1 in. square, the same segment will intercept 40 sq. in. (*EFGH*) on the wall of a concentric 20-ft. well. Hence the rate of flow of oil through section *ABCD* is forty times that through section *EFGH* and the pressure loss per linear unit of travel is correspondingly great. This assumes that all the oil passing *ABCD* also passes *EFGH*, which is not, of course, exactly true as the volume of flow increases as the well is approached. At section *IJKL*, on the circumference of the drainage area, the flow is theoretically zero and the area is 1200 sq. in. Because of the extremely low velocities in the outer half of the drainage area, the pressure loss is almost negligible. In Fig. 2, squares equivalent to the cross-sectional areas *ABCD*, *EFGH*, and *IJKL* are drawn to scale to indicate the relative size of the spaces through which the oil must move.

It is apparent that enlarging the well will increase the effective area through which oil enters, and as the pressure behind or within the oil is unaltered, the rate of flow will increase and a larger quantity of fluid will enter the well. The result is analogous to that obtained by enlarging the diameter of a pipe through which water flows. If the effective pressure remains constant, the larger pipe will deliver a greater quantity of fluid.

In applying the principle of the Poiseuille formula, Slichter[2] has computed the following equation for the flow of liquids through cylindrical tubes filled with sand:

$$Q = \frac{0.2012pd^2s}{ulK} \tag{2}$$

in which Q = quantity of fluid flowing, in cubic feet per minute; p = pressure drop, expressed in feet of water; s = area of cross-section of tube, in square feet; d = "effective diameter" of sand grains, in millimeters; u = absolute viscosity of fluid, in poises; l = length of drainage channel, in feet; and K = constant, depending on the porosity of sand.

From Slichter's results, the constant K varies greatly with the size of the sand grains. If o represents the percentage porosity, K will vary as some function of o; that is, $K = C_1\ o^x$. From Table III of Slichter's Field Measurements of the Rate of Movement of Under-

[2] C. S. Slichter: Theoretical Investigation of the Motion of Ground Waters. U. S. Geol. Sur. 19th Ann. Rept., part 2 (1897–98).

ground Waters,[3] it is possible to compute the value of the exponent for o, which enables us to write equation (2) as follows:

$$Q \quad \frac{Cpd^2so^{3.3}}{ul} \tag{3}$$

in which C = constant equivalent to $0.2012 \times C_1$. If L is taken as the radius of the drainage area of a well, r the radius of the well, and t the thickness of the oil sand from which it produces (all expressed in feet) we may integrate equation (3) to find an expression representing the pressure loss suffered by the oil in flowing into a well from the surrounding drainage area. The result will be:

$$P = C \log_{10} \frac{L}{r} \frac{Qu}{td^2o^{3.3}} \tag{4}$$

in which C is a constant differing from that in equation (3). Experimental data indicate that the value of C in equation (4) will be a quantity between 12,000 and 20,000.[4]

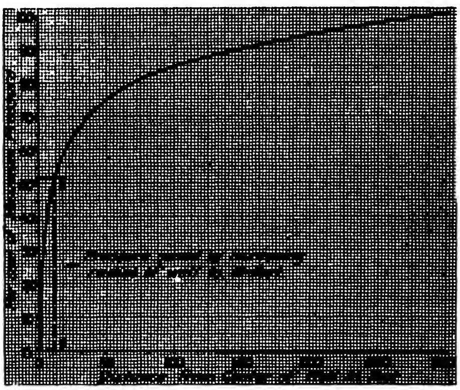


FIG. 3.

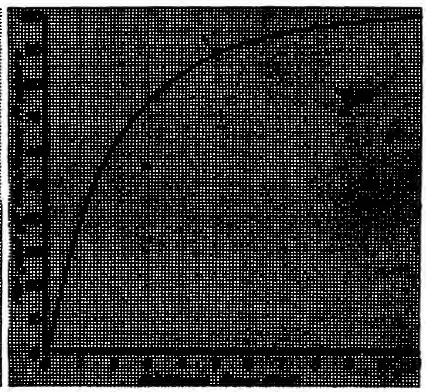


FIG. 4.

FIG. 3.—PRESSURE LOSS IN MOVING OIL THROUGH SAND INTO A WELL; DATA COMPUTED FROM EQUATION 4. AN EFFECTIVE DRAINAGE RADIUS OF 300 FT. AND A DIAMETER OF 6 IN. ARE ASSUMED FOR WELL.

FIG. 4.—PRESSURE LOSS IN MOVING WATER THROUGH SAND TO AN OUTLET 47 IN. BELOW FLUID SURFACE; UNIT OF DISTANCE, 12 IN. DATA OBTAINED BY EXPERIMENTAL METHODS AFTER F. H. KING IN 19TH ANNUAL REPORT, U. S. GEOL. SURVEY.

If we adopt values for p, u, t, d, o, and L in equation (4) and compute the flow into two wells, one having a diameter of 6 in. and the other a diameter of 20 ft., in a given time the 20-ft. well will produce approximately 2.1 times as much oil as the 6-in. well (see Table 1). This result accords in a general way, with conclusions reached by Slichter.[5]

[3] U. S. Geol. Sur. *Water Supply Paper* 67.

[4] From thesis of R. S. McIntyre, A Study of Factors Influencing the Underground Drainage of Oil Sands. University of California, 1924, conducted under supervision of author.

[5] *Op. cit.*, 362, 377.

It can also be demonstrated, by substitution in this formula, that the greater part of the pressure necessary to force the oil into a well is dissipated in overcoming resistance offered by the sand within its immediate vicinity. For example, the data for the curve in Fig. 3, computed from equation (4), shows that for a 6-in. well draining an area having a radius of 300 ft., 52 per cent. of the pressure is consumed in moving the oil through the zone within a radius of 10 ft. of the axis of the well, Fig. 4, plotted from results obtained by King,[6] shows a very similar graph representing the pressure loss in water-saturated sand in process of drainage. These values represent actual pressures recorded under experimental conditions.

TABLE 1.—*Computed Variation in Productivity of Wells of Different Diameters*

Radius of Well, Feet	Assumed Radius of Drainage: 300 Feet (Per Cent. Productivity)	Assumed Radius of Drainage: 150 Feet (Per Cent. Productivity)
0.25	100	100
0.50	111	112
1.00	125	128
5.00	175	190
10.00	212	236
15.00	241	278
20.00	265	316

EXPERIMENTAL EVIDENCE DEMONSTRATING ADVANTAGE OF LARGER DIAMETER WELL

To demonstrate in a quantitative way the advantage of the larger diameter well in securing a more rapid rate of production, the writer performed a small-scale laboratory test in a rectangular box filled with oil-saturated sand. One side of the box used (Fig. 5) is of plate glass so that the condition of the sand, the position of the drainage lines, and the oil surfaces are apparent at all times. Openings through the ends of the box provide connections with oil reservoirs A and *B*, which are kept full of oil. The sand, once saturated with oil, is maintained in this condition during pumping operations by oil flowing in from the reservoirs to replace that pumped out. The sand used was accurately sized material, 30- to 40-mesh. The oil with which the sand was saturated was a San Joaquin Valley, Calif., crude of about 19° Bé. gravity. The two "wells" used in pumping oil from the sand are shown at *C* and *D*;

[6] *Op. cit.*, 264.

their dimensions are shown in Fig. 6. Both were immersed in the sand to 9 in. below the top surface. A vacuum pump *P*, connected with heavy rubber tubing through an oil receiver *R* and a manifold of ¼-in. pipe with suitable valve control, was used to draw out as much oil as would enter the wells through the screens. Manipulation of the valves *U* and *V* permitted the application of suction to each well in turn,

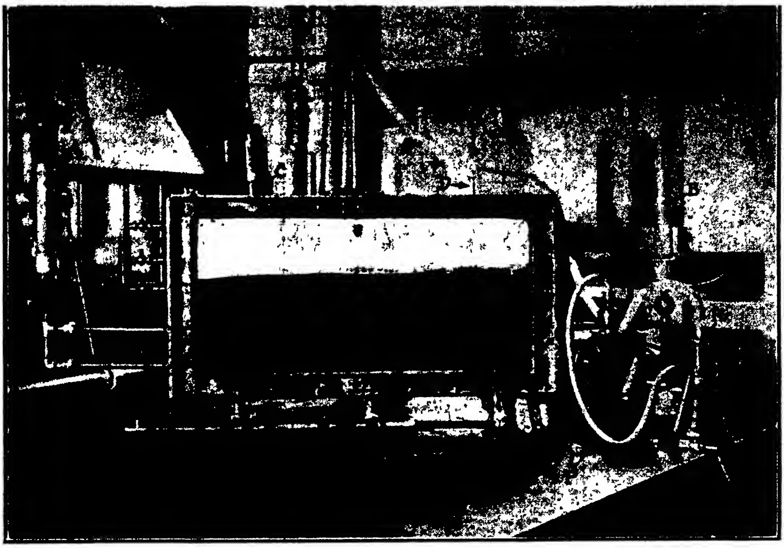


FIG. 5.—GLASS-WALLED BOX, SHOWING ARRANGEMENTS FOR PUMPING OIL FROM SANDS UNDER VACUUM.

under conditions that remained practically constant. Each well was pumped in turn for ½-hr. intervals, the volume of oil entering the receiving flask *R* being carefully measured in a graduated cylinder. The 0.7-in. well produced at an average rate of 133 c.c. per min., while the 1.7-in. well averaged 170 c.c. per minute.

Beneficial Effects Resulting from Increase in Diameter of Wells

From the foregoing mathematical and experimental data, it is evident that the productivity of a well will increase with increased diameter, and if by any practical means the diameter of the well within the oil sand could be increased from 6 in. to, say, 20 ft., the gas and hydrostatic pressure would be effective in at least doubling the productivity of the well. This increase in the rate of production would also increase the radius of drainage of the well and hence the gross production, for the reduced resistance to flow would result in the movement of oil over

greater distances. It must be remembered, in this connection, that the area drained by a well is not constant but decreases as the field pressure declines. While oil might move toward the well over a drainage area 600 ft. in diameter during the first year of productivity, when the field pressure is high, five years later, when the pressure has greatly declined, the area influenced by the well will be much smaller. The advantage of exhausting the well in the shortest possible time, therefore, is obvious.

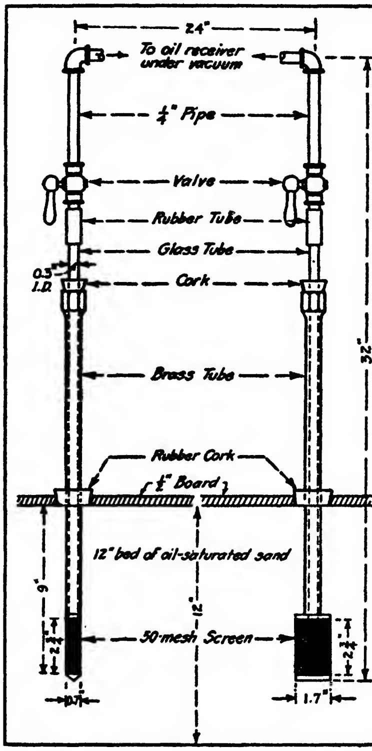


FIG. 6.—SCREENED TUBES USED IN PUMPING OIL FROM SAND WITH AID OF VACUUM.

Assuming that the initial year's production of a 6-in. well could be approximately doubled by increasing its diameter within the oil sand to 20 ft., the ultimate production would be greatly increased. For example, according to the U. S. Treasury Department's Manual for the Oil Industry, an average well in the Buena Vista Hills area, Midway field, Calif., having an initial year's production of 70,000 bbl. has a probable ultimate production of 234,000 bbl.; while a well having a production of 140,000 bbl. during its first year has a probable ultimate production of 378,000 bbl. This represents a gain of 144,000 bbl. through enlarging the well, which amount, because of the normal decline characteristics, is largely recovered during the first two or three years of pro-

ductive life. That is, its period of realization is short and its present value correspondingly high.

Whether the law of equal expectations on which the foregoing reasoning is based would hold when comparing a 20-ft. well with a 6-in. is, perhaps, doubtful; but even assuming that the large well produced no more oil than the small well, it would produce it in a shorter time, so that its present value would be greatly augmented and many years' operating expense would be eliminated. It seems reasonable to assume, however, that if the rate of production of a well is thus increased, the well will ultimately produce a larger quantity of oil, not only through the extension of its drainage area but also as a result of more efficient drainage. As the area of a circle increases as the square of its diameter, the radius of drainage of the well does not have to be greatly extended to bring twice as much oil within its influence. For example, a drainage area 850 ft. in diameter will contain twice as much oil as one 600 ft. in diameter. Increased efficiency of extraction alone would easily account for the enhanced production, bearing in mind the fact that by present methods of extraction in many cases we probably do not recover more than 25 per cent. of the oil present in the sands. In addition to the wider spacing of wells that the increased drainage radius would make possible, resulting directly in a lower cost of development for a given acreage, the advantage of an operator in competition with his neighbors along property boundaries, in being thus enabled to increase the rate of production and radius of drainage of his wells, is obvious.

Proposed Method for Increasing Effective Diameter of Wells

The foregoing discussion is purely academic and of no practical significance unless a means can be found of accomplishing the enlargement of the well to the desired diameter and, also, of supporting the walls of the enlarged well so that they do not cave. The sinking of a well from the surface 20 ft. in diameter to the depth from which present-day oil production must be obtained would be uneconomical and impractical. The only other alternative is to ream out a well of normal diameter to the desired size where it passes through the oil-producing stratum. Mechanical under-reamers intended for enlarging a well at depth, however, are limited to a few inches in their range of expansion, and no mechanical device that can be operated through a 6-in. well can excavate a cavity of such proportions as has been suggested.

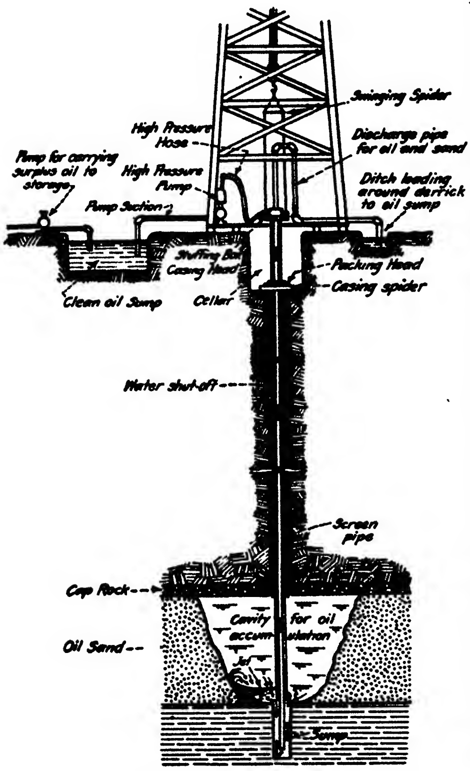
The process here described, which as yet is untried on more than a laboratory scale, the author believes will accomplish this result, at least in certain kinds of oil-bearing rock: particularly the loosely cemented oil sands characteristic of the California and some of the Gulf Coast and Mid-Continental fields of the United States. This process consists

in the erosion of the oil sand by a high-pressure hydraulic jet of oil directed from tubing lowered through the well, subsequently filling the cavity thus formed with gravel to support the walls and prevent their caving. By the method proposed, under favorable conditions, it is considered feasible to excavate a cavity about the well that will average 20 ft. or more in diameter and extend throughout the entire depth of the oil-producing stratum. The well will be filled with oil so that the detrital material loosened by the jet will be carried to the surface by the oil from the jet, the oil being circulated continuously through the well in much the same manner as is mud fluid in rotary drilling. After the cavity is formed, and while its walls are prevented from caving by the hydrostatic head of oil within the well, fine gravel or carefully sized crushed-rock fragments about ¼ or ⅜ in. in diameter will be pumped into the well with the circulating oil until the cavity is again filled. The walls of the cavity will thereby be prevented from caving when the fluid is removed, while the comparatively large interstices between the pebbles will offer small resistance to the flow of oil, so that the enhanced productivity of the well resulting from greater effective diameter will not be greatly altered. All of this work is done after the well has been drilled to its full depth and completed according to the usual present-day practice.

Forming the Cavity

The equipment it is proposed to use in circulating oil through the well is shown in Fig. 7, while Fig. 8 is an enlarged view of the tubing lowered into the well. Two concentric strings of tubing *C* and *D* are used, the inner tube *D* having smooth oxyacetylene welded joints at its lower end so that it is free to slide up and down within the metal plug *F* closing the lower end of the outer pipe *C*. This plug fits snugly about the inner pipe *D*. Both tubes are lowered into the well, first the outer pipe *C* and then the inner *D*. The outer tubing is supported in the derrick by a swinging spider of the type used in supporting casing in circulating while drilling with the cable tools; its lower end is about 50 ft. off bottom. The inner pipe *D* passes through the plug *F* and extends to within 1 or 2 ft. of the bottom of the well; it may be supported in stationary elevators suspended in the derrick. It is assumed that the well has completely penetrated the oil sand and has been drilled 10 or 20 ft. into the underlying formation. All openings between the conductor and outer strings of casing are effectively closed with one or more packing heads. A stuffingbox casing head is placed on the outer pipe *C*, the inner pipe *D* projecting through it into the derrick; the upper two or three joints of this pipe *D* also are welded with smooth joints. Pump connections are made through an armored high-pressure hose with one side outlet of

the stuffingbox head on pipe *C*. The pump may be of the type commonly used in circulating mud fluid in rotary drilling and should be capable of developing a pressure of 800 or 1000 lb. per sq. in. Connections are made from the top of the inner pipe *D* to a sand-settling trough by means of which the oil circulated through the well is led to an oil sump, whence it is taken up by the pump suction for further circulation. The swing-



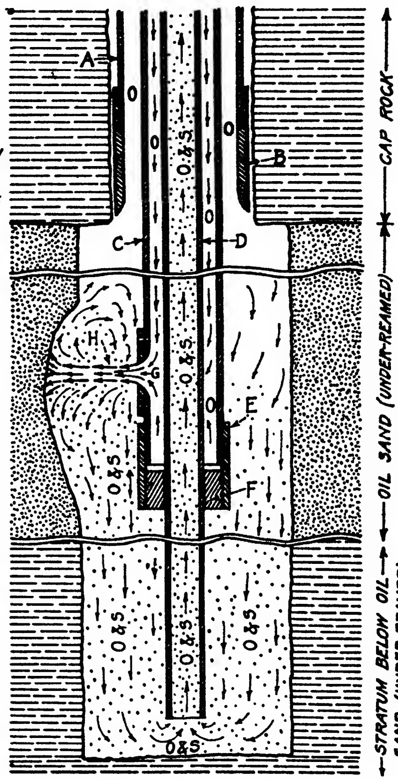


FIG. 7. FIG. 8.

FIG. 7.—ARRANGEMENTS FOR FORMING A CAVITY ABOUT A WELL BY HYDRAULIC ACTION OF A JET OF OIL.

FIG. 8.—METHOD OF FORMING A CAVITY ABOUT A WELL BY HYDRAULIC ACTION OF A JET OF OIL; *O*, OIL; *O & S*, OIL AND SAND.

ing spider permits the outer pipe *C* to be raised or lowered with the aid of the power, without altering the position of the inner pipe *D*; with the flexible pump connection it is also possible to turn pipe *C* about pipe *D*, back and forth through 360°.

Oil is pumped down between the pipes *C* and *D*, flows under high pressure through an orifice *G* near the lower end of the outer pipe *C*, and is jetted directly against the oil sand forming the walls of the well (see Fig. 8). Though its force will be partly absorbed by the oil with which

the well is filled, it is thought that the pump pressure of, say, 800 lb. per sq. in. will have a considerable erosional effect even though the sand face is 8 to 10 ft. distant. By raising or lowering this pipe *C* with the swinging spider, or turning it on the inner pipe *D*, as an axis, from the surface, the jet may be raised or lowered and directed against all parts of the oil-sand face exposed within the well.

Oil is returned to the surface through the inner pipe *D*, the lower end of which is maintained but 1 or 2 ft. above the bottom of the well. Detrital material loosened by the jet settles into the sump below the oil stratum and is swept upward to the surface into the sand-settling trough; the oil drops its sand and is discharged into the oil sump for further circulation.

When forming a cavity by this method, advantage may be taken of the tendency of the oil sand to cave by starting the cavity at the bottom of the oil stratum and working upward. Because of the tendency of the material to seek its angle of repose, the diameter of the cavity at the top may be somewhat greater than at the bottom. Circulation and manipulation of the oil jet might be continued until sand no longer flows to the surface with the circulating oil, thus indicating that the practical limit of the effective force of the jet has been reached. During the early stages, it will probably be desirable to use a reduced pump pressure to avoid loosening the sand more rapidly than it can be removed by the circulating system. However, the circulating system will be capable of taking care of large quantities of sand, as the sand does not pack when suspended in oil and a large percentage may be present without greatly influencing the fluidity of the mixture.

Filling the Cavity

Sometimes, in the case of a partly cemented oil sand, the cavity thus formed about the well will remain open, the walls displaying little or no tendency to cave. In such cases, the well may be placed on production as soon as the cavity has been cleared of accumulated detrital material. When dealing with unconsolidated oil sands, however, which readily cave as soon as the hydrostatic head within the well is removed, it will be necessary to fill the cavity with a porous, sustaining medium before the oil in the well has been bailed or pumped out. For this purpose, carefully sized gravel or crushed rock fragments about 1/4 in. or 3/8 in. in diameter may be used. Slichter[7] has shown that a fluid will flow about 2500 times as fast through fine gravel about 1/5 in. in diameter as it does through very fine sand (about 150 mesh), even though the two media have the same percentage porosity; hence the oil will meet with but little resistance when moving through the well cavity to the tubing.

The equipment used to excavate the cavity could subsequently be used to place the gravel, with some additional features in the surface equipment. In Fig. 9, *I* and *J* are cylindrical gravel containers supported above the stuffingbox casinghead *K*, and connected with the pipe *L* through which oil is pumped into the space between the pipes *C* and *D*. The two containers are supported on rollers so that they may be revolved with the pipe *C* when manipulating the jet. The pumps and circulating fluid are operated in the same manner as described for the formation of the cavity, except that the outlet pipe *D* is closed and the oil flows back to the surface between the outer pipe *C* and its conductor casing *A*. However, a lower pump pressure should be used when pumping gravel than when excavating so as to avoid loosening additional sand, which would settle between the interstices of the gravel and reduce its effective porosity.

The gravel containers *I* and *J* are equipped with suitable valves *M* and *N* where they make connection with pipe *L*; other valves *O* and *P* are placed at their upper ends. With the upper valves closed and the lower valves open, the interior of the gravel containers may be maintained under the full pump pressure and in direct connection with the oil-circulating system. Gravel of suitable size to pass freely through the valves, and between pipes *C* and *D* and through nozzle *G*, is charged into the containers *I* and *J*, the upper valves *O* and *P* are closed, and either valve *M* or *N* is opened. With the pumps working under moderate pressure and with oil flowing down between the pipes *C* and *D*, out into the well cavity through the nozzle *G*, and back to the surface between the outer pipe *C* and the conductor casing *A*, gravel enters the circulating system, is swept down through the annular space between the pipes *C* and *D*, through the nozzle *G*, and is deposited in the well cavity. If the volume of the circulating fluid is so adjusted that the oil flowing back to the surface has not sufficient velocity to lift the gravel, it will accumulate in the bottom of the cavity until the latter is filled. By securing a proper ascending velocity of the oil during its return to the surface between the pipes *C* and *A*, it will, through its sorting action, carry to the surface any sand, clay, etc. that may be dislodged from the walls of the cavity during deposition of the gravel, leaving the latter free of such material. If the sand tends to cave during deposition of the gravel, a second pump may force a stream of oil down to the bottom of the well through the inner pipe *D*. If the velocity of this stream is carefully adjusted, it will, on circulating up through the gravel during deposition, carry the loose sand to the surface, leaving the interstices of the deposited gravel free of sand.

When placing the gravel, the jet is first lowered to a point near the bottom of the cavity and then raised slowly and turned back and forth as the gravel accumulates. The gravel containers *I* and *J* are connected

with the circulating system alternately, one being filled while the other is feeding its material into the well. They may be readily refilled from a loading apron, which is filled with gravel on the derrick floor, hoisted into the derrick above the containers, and connected with the valve of the container to be filled.

In some cases, it may be feasible to fill the well cavity by gravity, merely dumping gravel into the inner pipe *D*, raising both pipes *C* and

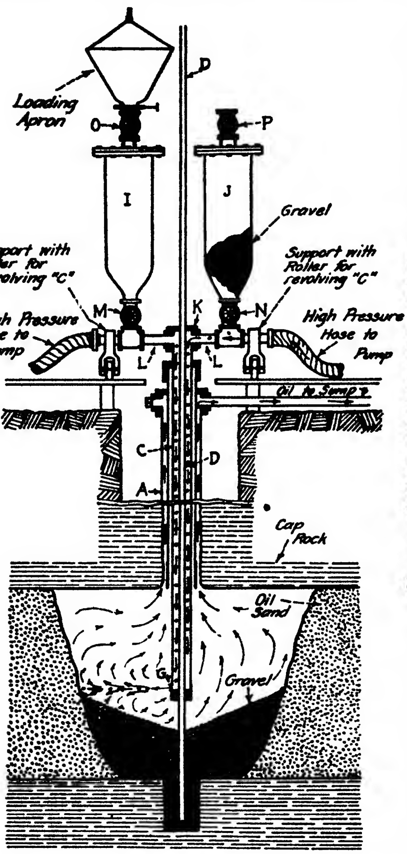


Fig. 9.

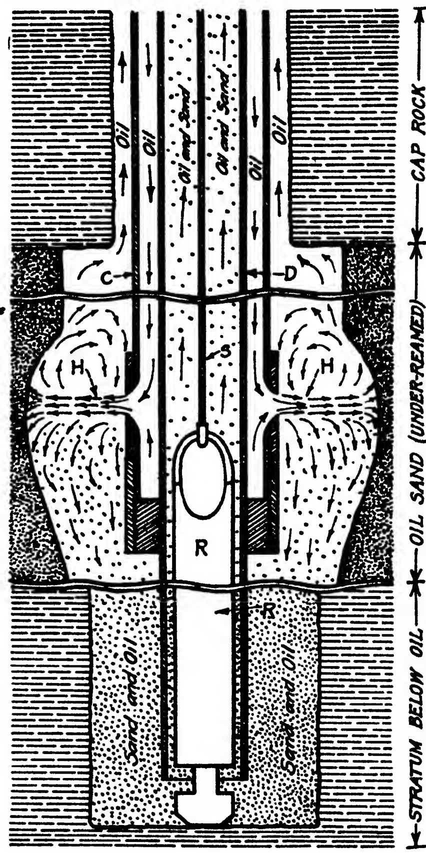


Fig. 10.

Fig. 9.—Arrangements for filling a cavity about a well with gravel by hydraulic action of a jet of oil.

Fig. 10.—Method of forming a cavity about a well by hydraulic action of jets of oil; detrital material removed by circulating or bailing.

D as the gravel accumulates; but in view of the difficulty of settling a large quantity of gravel to the bottom of a deep well through a tube only a few inches in diameter, and filled with viscous oil, placing the gravel with the pump pressure may be preferable. Furthermore, the angle of repose of the gravel might not permit the complete filling of a shallow

cavity of large diameter by gravity. If the gravel is placed by gravity, occasional tamping with the cable drilling tools during deposition will aid in working it out to the walls of the cavity.

After the well cavity is completely filled, the pipes *C* and *D* are withdrawn and the screen pipe *A* is lowered to the bottom. Some of the gravel may cave into and partly fill the hole left by withdrawing the pipes *C* and *D*, but this material will be readily pushed aside by the shoe of screen pipe *A* as it is lowered to the bottom of the cavity. Any gravel remaining within pipe *A* after it is placed on bottom may be bailed out with a sand pump. The permanent pumping device can now be lowered within the screen pipe and the well placed on production.

Supplementary Methods for Special Cases

Should it be found impossible to secure circulation of oil back to the surface, because the sands exposed within the well absorb oil more rapidly than it can be pumped in, other means of removing the detrital material must be adopted. It may be feasible to remove the detached sand by bailing, or by a compressed-air lift or ejector. Arrangements for bailing are shown in Fig. 10, which shows the application of two jets placed 180° apart on pipe *C*. Oil is pumped down between pipes *C* and and *D*, as before, and forced through the jets *H* against the oil sand, gradually eroding it away. It is assumed that oil accumulates in the well until it attains a sufficient head to cause the oil sand to absorb it as rapidly as it is pumped in. It is thought that this will rarely happen, but it may result in attempting to form cavities in partly exhausted oil sands, the circulating oil entering the oil sand to fill voids left by oil previously extracted. The sand loosened by the jet sinks to the bottom of the well and is removed by the bailer *R*, which is operated through the inner pipe *D* on sand line *S*. The bailer must be operated continuously and lowered to the bottom for its load. Pipe *D* should, with this method, be as large as the diameter of the well will permit and the bailer *R* should be as long as possible in order to secure maximum capacity.

Under certain conditions, it will be feasible to remove accumulated oil sand from the well with a compressed-air lift or ejector. The ability of the air lift to handle large quantities of fluid and suspended sand in oil wells has been demonstrated in many instances.[8] A reasonable submergence, preferably 30 per cent. or more of the total lift, must be secured for efficient operation; that is, the oil used in operating the jet must accumulate in the well to some such depth above bottom. If the well has been drilled to a sufficient depth below the oil sand to secure the necessary submergence, it might be feasible, with the aid of the air lift,

[8] L. C. Uren: "Petroleum Production Engineering," 370–377. McGraw-Hill Book Co., New York, 1924.

to maintain a fluid level in the well below the position of the oil jet, so that the latter can apply its full force directly against the oil sand without, having its energy partly absorbed by the surrounding fluid. The effective force and range of the jet will be greatly increased in such a case but conditions favorable for such a method will be found only in comparatively shallow wells. The maximum air pressure available with two-stage compressors (ordinarily about 500 lb. per sq. in.) will limit the depth of operations to about 3000 ft., assuming a submergence of about 1100 feet.

Of the three methods proposed for removing the oil and sand from the well, the first method is the most practical and easiest to apply. The well equipment may be readily installed and the method presents no unusual problems. If the well has been drilled by the rotary method, the oil pump used to provide pressure, the oil sump and sand-settling trough may be those used in circulating mud fluid during the drilling of the well. The swinging spider, special casingheads and gravel containers may be readily assembled and moved from well to well and rigged in a short time. If circulation cannot be established, because of rapid absorption of the circulating oil by the oil-bearing stratum, the bailer method or the air-lift method may be employed. The bailer method, however, will have but limited capacity for sand and fluid; and the air lift will require costly compressor equipment and air transmission facilities not ordinarily available on oil-producing properties.

The most advantageous method of applying the jet and of filling the cavity will vary with different wells and a careful study of the conditions to be met should be made in each individual case. The time at which the work should be done will also be an important consideration. If gas pressure is high during the early life of the well, the difficulty of keeping the well under control will make it advisable to defer excavation of the cavity until the pressure has subsided. On the other hand, if the well has been producing for some time, it may be difficult or impossible to loosen the perforated "oil string" in order to get access to the sand. In such a case, it will be necessary to "side track" the lower part of the oil string and redrill the well through the productive stratum. A side-tracked column of casing may interfere with the action of the jet to some extent but need not necessarily prevent a satisfactory result. Application of the oil jet against the perforations with occasional swabbing, or circulation under the shoe and through the perforations with a wash pipe and plug, will aid in loosening a frozen oil string.

Possible Difficulties in Application of Proposed Process

One or more uncertain points have probably suggested themselves to the reader in connection with the procedure outlined above. How

will the oil sand react under the influence of the hydraulic jet? Will the force of the jet, partly spent in overcoming resistance of the well fluid, be inadequate for the purpose and fail to secure the desired range of action? Will the jet loosen the sand so rapidly that the lower portion of the well and ejector tube will become "sanded up?" Will the cavity cave as rapidly as formed; that is, will the hydraulic head maintained within the well be ineffective in preventing caving before the cavity can be filled with gravel? The author believes that, with varying types of oil sand, any one of these occurrences might prevent successful accomplishment of the desired result. If the oil-bearing stratum is a hard, firmly cemented sandstone, the radius of action of the jet will probably be small. If the sand is unconsolidated and uninfluenced by cementation, it may display a tendency to cave during the formation of the cavity; and continued caving with possible subsidence of the cap rock may lead to serious consequences. Granting that such may be the case, with extremes in the degree of cementation of the sand, there are still intermediate types or partly cemented oil sands with firm cap rocks, in which the process would be successful. In such cases satisfactory progress of the work would depend merely on good engineering and skill in control and manipulation of the equipment. It is possible that even the more difficult types of oil sand can be successfully handled after the mechanical technique of the process has been perfected.

The effective range of action of the hydraulic jet in excavating a cavity about a well will be influenced, to some extent, by the depth at which it is applied. The pressure impressed on the circulating oil and transmitted thereby to the jet will be partly consumed in pipe friction during its circuit through the well; it must also furnish the lifting force to remove the sand detached from the walls to the surface. The net pressure, after making these deductions, will determine the effective range of action of the jet in the work of excavation. The jet will probably lose all semblance of definite form within a few feet of the orifice by which it is formed, because of turbulence induced by the surrounding fluid; but the momentum of the stream will produce a considerable erosional effect at a much greater distance.

A somewhat difficult problem in design is the determination of the desirable diameter for the jet orifice, in terms of the volumetric capacity of the pump when operating at the maximum available pressure. If two slush pumps are available, as will be the case with a rotary drilled well, both may be used, arranged to operate in parallel in order to increase the volume of flow. Care must also be taken in selecting the sizes of tubing to be used. The annular space between the two tubes must be sufficient to pass the desired volume of descending fluid without undue pressure loss, and the inner tube must be of such size that an adequate ascending velocity for the sand-laden oil will be assured.

Operation of Proposed Process on an Experimental Scale

In an effort to find an answer to some of these questions, the author performed an experiment in the glass-walled box (Figs. 5 and 11). The box was filled to a depth of 12 in. with a carefully screened beach sand of −50, +60 mesh. The sand was then saturated with a California crude of about 19° Bé. gravity. Two wells were excavated in the sand, one of which was 0.7 in. in diameter and cased with a brass tube and screen similar to that illustrated in Fig. 6. The second well was made 1.7 in. in diameter. Though left uncased, it displayed but little tendency to cave during the entire progress of the experiment. Both "wells" were filled with oil to the surface of the sand, as the sand was saturated with oil and maintained so by direct connection with oil reservoirs at each end

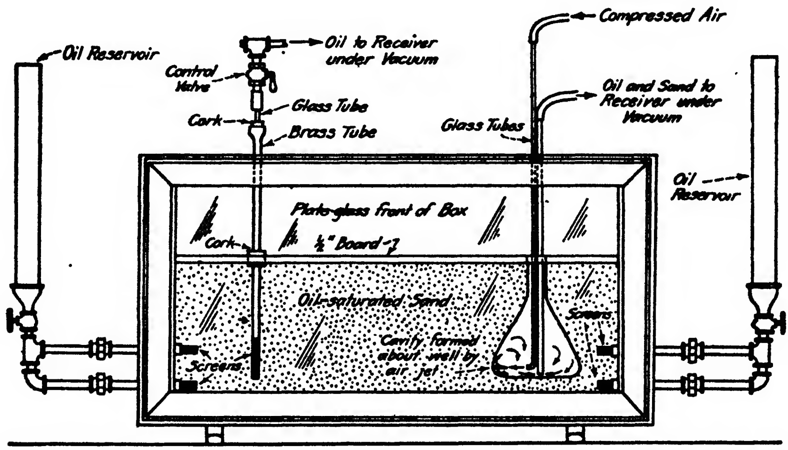


Fig. 11.—Manner of conducting laboratory tests in glass-walled box containing unconsolidated, oil-saturated sand; at right, method of forming a cavity with aid of a compressed-air jet; at left, arrangements for pumping under vacuum.

of the box. In the larger, uncased well, two small glass tubes were placed: one ⅛ in. in diameter with a short nozzle bent at right angles at the lower end, through which compressed air under 2 or 3 lb. pressure was forced; and the other a straight tube about 0.3 in. inside diameter, which was connected at its upper end, by rubber tubing through an oil receiver, to a vacuum pump. The compressed air served to loosen the sand as would an oil jet, while the vacuum pump removed oil from the hole, carrying the suspended sand detached by the jet. The miniature jet was maintained at a depth of 9 in. below the sand surface and was slowly revolved so that it directed its force successively in all directions in its horizontal plane. The sand about the jet was rapidly eroded away, but was readily extracted and prevented from accumulating in the well by the vacuum pump, oil flowing into the well from the sand to provide

the necessary suspending medium. Eventually the cavity was extended out to the glass side of the box, through which its form could be studied; Fig. 11 illustrates the result. Though the sand "roof" overhung the cavity at a considerable angle from the vertical, it displayed no tendency to cave and the pear-shaped cavity was maintained without any support other than the oil in the hole. After excavating the cavity, a brass tube 0.7 in. in diameter, similar to that illustrated in Fig. 6, equipped with a cylindrical screen at its lower end, was inserted in the cavity to a depth of 9 in. below the sand surface. The space about the screen pipe within the well and the enlarged cavity was then filled with angular fragments of crushed rock of about 6-mesh size. This material was simply poured in about the brass tube from the top.

On completion of the foregoing, there were two brass tubes equipped with screens of identical proportions embedded in the oil-saturated sand to the same depth. In one case, however, the sand was in immediate contact with the screened tube, while in the other case the tube was surrounded by a pear-shaped cavity filled with crushed rock, the cavity being about 4 in. long and 4 in. in diameter at its lower end. Pumping tests were next made to determine the comparative productivity of the two "wells," using a vacuum pump to suck out the oil from each of the two wells alternately, as in the previous experiment. The 0.7-in. diameter well, in which the sand was directly in contact with the screen tube, produced at an average rate of 52 c.c. per min., while the well surrounded by the rock-filled cavity produced at the rate of 106 c.c. per min., thus demonstrating conclusively the greater capacity of the enlarged well.

Location of Well Cavity in Thick Oil Sands

In the application of the process in thick oil sands, it would probably not be necessary to enlarge the well for the full thickness of the oil-producing stratum. Because of the rapid depression of the fluid level in the immediate vicinity of the well, only the lower portion of the oil sand would be productive of oil; and if the well cavity were confined to this region, the rate of production would probably be as great as if it extended up to the cap rock; this is illustrated in Fig. 12. If edge water is present in the oil sand in the vicinity of the well, however, the oil will be floated to the top of the oil stratum, and the well cavity, in order to be effective, must be placed immediately below the cap rock. If water in the oil sand is likely to be a factor, uncertainty regarding its effect at various periods in the well's future history would make it advisable to enlarge the well through the full depth of the productive sand.

Screening Effect of Gravel or Crushed Rock

An advantage that might reasonably be anticipated for a well surrounded by a cavity filled with gravel or crushed rock would be the screening effect of the gravel in preventing sand from entering the pumping device used in lifting the oil to the surface. Experiments performed by the author have indicated that, even with unconsolidated 50- to 60-mesh sands under pressures as high as 50 lb. per sq. in., little or no

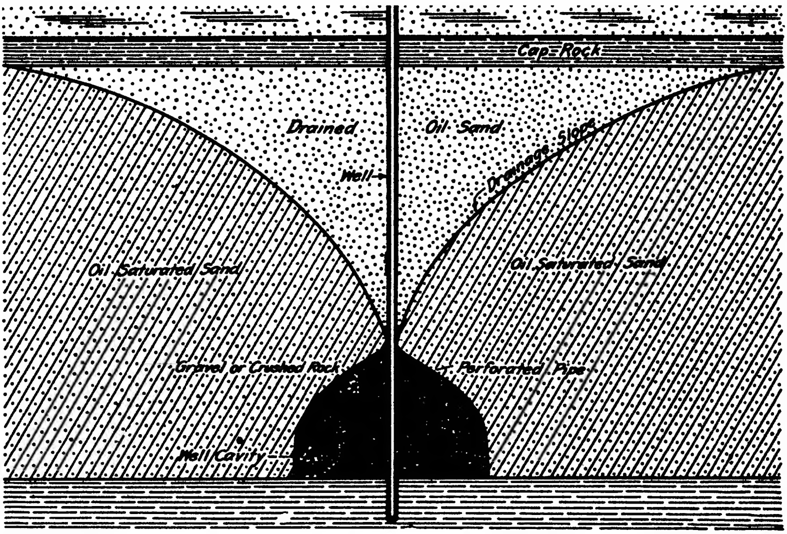


Fig. 12.—Position of a gravel-filled cavity about a well to drain a thick oil sand; because of depression of fluid level in region of well, only lower portion of sand is productive; water is assumed to be absent.

sand will find its way into the closely packed body of gravel filling the well cavity. The operator would, therefore, be entirely relieved of the many annoyances and loss of operating time occasioned by wear and "sanding up" of the pump, the clogging of screens and other difficulties occasioned by the presence of sand. It is considered feasible when this process is used, to surround the tubing and pump with a shop-perforated pipe, without screens of any sort. If of slot form, the perforations may have a width as great as twice the diameter of the gravel pebbles.[9] Such a liner would admit oil freely to the pump, and yet would hold back the gravel so that the pump could be withdrawn for repairs when necessary.

[9] F. A. Graser: Thesis on A Study of the Screening Effect of Slot Openings in Unconsolidated Sands. University of California, 1924; conducted under the supervision of the author.

Analogies and Anomalies in Existing Practice

It has long been the custom of oil producers to "shoot" oil wells producing from hard and close-grained reservoir rocks, so as to form cavities and fractures about the wells, but no similar practice has been developed by operators in the fields deriving their production from unconsolidated sands and soft sandstones. While many observers have noted the increased productivity of wells operated in such a way as to encourage the production of large quantities of sand with the oil,[10] the reasons for the increased flow of oil as a result of this practice seem not to have been generally understood; and there has been little or no effort to develop a process that would result in the formation and maintenance of cavities about the wells. In fact, most operators have adopted the policy of holding back as much of the sand as possible in the hope of preventing the formation of cavities. The reasons for doing so are, primarily, to avoid the mechanical difficulties involved in pumping large quantities of sand with the oil, and the effects of subsidence, caving, and shifting of sands about the well casings. It is thought that the method herein proposed, involving initial formation of the cavity before pumping is begun, with subsequent maintenance of the walls to prevent caving, will largely offset the difficulties that have hitherto been experienced.

Summary and Conclusions

In this paper, the increase in rate of production of oil from wells with increased diameter is demonstrated from both the physical and mathematical points of view and by experimental evidence.

The advantages resulting from this enlargement of the well through increase in the rate of productivity are pointed out, the gross or ultimate production being greatly increased. Because of the wider spacing of wells made possible by the increased radius of drainage, a considerable reduction in development expense may be effected. Because of the more effective exclusion of sand from the well by the gravel-filled cavity, there will be less time lost in repair work; hence production will be increased and operating costs reduced.

A process for enlarging wells where they penetrate oil sands, through the action of oil jets directed under pressure against the walls of the well, is proposed. If the walls of the cavity thus formed within the oil sand show a tendency to cave, they may be supported by filling the cavity with gravel or crushed rock, which will offer comparatively little resistance to the movement of oil. The porous medium with which the cavity is filled may also be placed with the aid of the hydraulic jet, using crude petroleum as a circulating medium.

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[10] W. H. Kobbe: Problems Connected with the Recovery of Oil from Unconsolidated Sands. *Trans.* (1917) 56, 799.

Experimental evidence is produced illustrating the application of the proposed process on an experimental scale and the increased recovery resulting from its application is demonstrated by comparative pumping tests which show a marked advantage for the enlarged well.

DISCUSSION

A. Beeby Thompson, London, Eng. (written discussion).—The subject discussed in this paper has long been debated by operators in European fields, where very strong views are held regarding the advisability of controlling gas pressures by shutting in wells. While unwilling to theorize on the subject of restricted flow, the writer has always been disposed to associate himself with those who hesitate to impose any obstruction to a natural transitory state that breaks up the oil-containing strata and establishes a feeder system which no subsequent events, natural or artificial, can approach in intensity. In both Russia and Roumania, where the oil is concentrated in discontinuous, disturbed, and irregular lenticles of sand varying, within short distances, in coarseness of grain, extent of impregnation and degree of cementation, it has been the practice to let the wells run wild in order to provoke disruption of strata. By encouraging violent eruptions, an extended feeder system is created and the ejection of enormous quantities of sand, rock, and clay creates a sump and seepage area that it would be difficult to imitate by any artificial means, not excluding actual mining.

Before discussing the somewhat novel method suggested for enlarging the infiltration area, the writer would like to confirm the fact that many valuable data applicable to oil are forthcoming from a study of water phenomena. Long association with water-supply problems in many parts of the world has shown how closely the phenomena of underground movements of water and oil are related, so that it is pleasing to note the author's use of water formulas. But there is one great distinction; whereas, in the case of water, underground phenomena can often be observed in workings and shafts, oilfield phenomena can only be conjectured, except in rare and unusual circumstances. Subjected to disintegrating influences, outcropping oil and water strata do present features comparable with those at depths below the water table of the district, and often below sea level. Fortunately, the mining operations in the Pechelbronn and Wertze oilfields of Alsace and Hanover have enabled the underground conditions of oilfields to be observed at leisure and in comfort; and to the writer it was interesting to note how correctly the conditions had been diagnosed from merely surface phenomena and reasoning. In these mines, the extent of depletion and the old channels of movement can be seen, and drainage can be watched in operation at great depths.

The importance of enlarging the diameter of wells to secure increased yields has always been fully appreciated by hydrologists; for which reason, where conditions admitted and the rocks were compact and not free yielding, it was preferable to excavate large-diameter wells. Not only was a larger infiltration area thereby provided, but a sump was produced in which water collected in bulk during periods when pumping was suspended. When excavating in light sands, it is always noticed that while water oozes from the exposed face of a saturated sandstone, the useful supplies are obtained mainly from cracks and fissures or coarser streaks, and that, unless such disrupted rock or coarser bands are struck, the yield of water is very slow and small. Exactly the same feature is noticeable in the oil mines. As new faces are exposed in the galleries, frothy oil may be seen spurting from cracks and fissures whereas on the unbroken face of the sand there is scarcely any outflow of oil.

In water work, we are familiar with a type of well that, on penetration of a light sand, fills with water and flows but will yield no greater quantity of water even if bailed or pumped dry. Such wells often have a static head far above the surface. The only apparent explanation is that the pore friction in the sand is sufficient to maintain this head at such a value that a lowering of the water level has no appreciable influence on the rate of outflow from the sand. The writer has met many oil wells that exhibit the same peculiarity. When left they gradually fill and flow slowly at a regular rate per day, but if pumped dry and kept dry by pumping there is no increase of yield. An enlargement of the hole would undoubtedly lead to some increase of yield, but this increase is of small importance unless it results in the penetration of a zone of fracture which, by its nature, must present a seepage area far in excess of any enlarged diameter. For this reason the writer considers that a much more effective increase would result from more violent methods that would make themselves felt over a wide area and probably establish connection with a fissure system or zone of disturbance.

In many cases of loose sands, the proposed conditions of gravel fill are naturally reproduced and play an important part in sustaining yields and establishing equilibrium. Most of the violent eruptive wells of Russia and Rumania expel enormous quantities of sand as well as abundant rock fragments in their initial life, thereby preparing a sump of considerable capacity somewhere below and not distant from the shoe of the casing, but a time is reached when the flows are less violent and only sand is ejected with the oil. Detached rock fragments that have collected in the well are kept in a state of agitation by gas, rounded, and in time form a rubble heap that while protecting the roof and walls of the oil bed from further destruction, permits the oil to flow freely to the well.

Both mechanically formed balls and nodules from the sands collect in large quantities around some of the violent Baku gushers; indeed many

tons have been extracted when repairing or deepening such wells at a later period. So far has this effect extended that new wells drilled within about 100 ft. of a gusher have penetrated these rubble masses. Much the same features are developed in the Rumanian oilfields, and in both fields dangerously violent eruptions of rock, shale, and sand occur between successive cleaning operations before oil in any considerable quantity enters the well. Months are sometimes spent in patiently dealing with these inrushes of material before free communication is established with the main oil sand and oil enters in any important quantities.

An interesting conflict of views recently occurred during the developing of a new rich field in Rumania. Violent eruptions of sand and rock fragments were seriously endangering the safety of the wells, yet the fear of checking the action before free communication was established with the main body of oil sand made the management hesitate to control the flows and thereby minimize the risk of loss of the well through collapse of the casing. Eventually pieces of the heavy shoe and torn casing were expelled with the mineral fragments, yet the chief could not be prevailed on to check these outbursts by controlled flow. It was simply a question as to whether the casing could resist the gas pressure until the underground disruption ceased, and for a time the result seemed very uncertain. Fortunately the casing outlasted the disruption of strata and the well came in as a very large producer, having prepared for itself an adequate feeder system.

There is too little information available to say whether controlled discharge under European conditions will supersede the oil practice of uncontrolled flow. It is often a contest between casing and uncalculable forces deliberately provoked in the hope that the casing would resist the enormous stresses it is often called on to sustain. In a large number of cases, the wells are either faced with irreparable damage or lengthy and costly repairs, so that this factor must not be overlooked when considering the relative merits of the two methods. Long before the law of equal expectation was propounded, the principle was admitted in Russia and Roumania, and a recognition of this law compels the admission that unrestricted flow and so high initial production will result in largest ultimate yields.

Various American writers have, however, questioned the usefulness of restricted flow and gas conservation, and some recent notes by J. M. Sands on Burbank Developments[11] are interesting reading. The value of shattering tight sands has been repeatedly demonstrated in numerous American oilfields where torpedoing is practiced; in water wells the results are often almost equally as important, although there is no gas to facilitate the expulsion of the liquid from the rock.

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[11] *Bull.* Am. Ass. Petrol. Geol. 8, 5.

As a result of repeated experiments to increase the yield from tight sands, the writer has found violent methods the most satisfactory. Improved yields have been attained by forcing gas, air, oil, or water into the strata and then releasing the built-up pressure or bailing out the liquid; varying results have been attained by applying a partial vacuum and important results have been reached by violent swabbing; but shooting has proved the most efficacious in harder sands. The writer, therefore, believes that while the method proposed by the author may prove useful for cleansing and revivifying wells of certain types, the best way of securing maximum yields in loose-sand fields is to submit to the trouble and remove as much sand as possible in the early stages, when the natural-gas pressure can be utilized to establish long distant connections with the well. The employment of sand screens is probably essential at times to ensure economic exploitation of the sands because of excessive mechanical difficulties, but most European technologists agree with the author that a large percentage of the oil would prove unrecoverable if obstructions were placed against the free entry of sand with the oil.

Lester C. Uren (author's reply to discussion).—This discussion is most welcome; particularly as it represents the European viewpoint which, as stated, is not wholly in agreement with American practice. While adhering to the principle that maximum oil yield is obtained through gas conservation, the author is disposed to accept that part of the discussion bearing on the advantages of unrestricted flow without further discussion, as he feels that it does not bear directly on the theme of this paper. The author would consider the application of the proposed gravel-filled cavity process inappropriate for a newly completed well still under high pressure, and would prefer to apply the process to such a well at some later date, after the pressue had subsided somewhat and the feeder system of crevices and fractures tributary to the well had been cleared by natural means. Enlarging the well cavity would be effective in increasing flow at any stage and the principle applies whether flow is regarded as occurring uniformly throughout the cross-section of thick oil sand or through crevices or channels.

In the case described by Mr. Thompson, in which a water well was pumped dry without increase in flow, the author believes that the well's production would be doubled if a cavity 20 ft. or more in diameter could be formed and sustained about it; and this would be true whether the well were producing oil or water. In the case of oil, however, there is a greater "draw-down" effect in the vicinity of the wells than in the case of water, because the greater visrosity of the oil creates more resistance to flow through the sand.

The author regards the description of the natural formation of rubble masses at the bottom of the more prolific Russian and Rumanian wells

as an interesting corroboration of the principle with which the paper under discussion deals. Where conditions are such that rock-filled cavities about the wells will form naturally, there is, of course, no necessity for attempting to create them by artificial means. It seems improbable, however, except in unusual instances, that the oil sand will contain gravel and rock fragments of proper size to form an effective screen for the particular size of sand in which they are embedded. It should be understood, in this connection, that the finer sand must be kept out of the gravel mass, otherwise no advantage is secured, and effective screening of sand from the gravel mass requires careful proportioning and uniformity in size of gravel used. Naturally formed gravel masses would seldom attain the required degree of uniformity and would seldom be formed of the proper size of fragments to prevent extraneous sand from permeating the mass as a result of the carrying effect of the flowing oil. On the other hand, this can be effectively accomplished in the case of the artificially formed gravel-filled cavity.

Significance of Fluid Level in Oil-well Pumping

BY LESTER C. UREN,* BERKELEY, CALIF.

(New York Meeting, February, 1925)

IT IS realized that the depth of fluid maintained in a pumping well is sometimes influenced by other considerations than the quantity of fluid that will enter the well: the prevention of sand incursion, prevention of waste of natural gas, and the maintenance of a suitable submergence for the pump, for example. These latter factors have an important influence on the productivity of the well, so that otherwise unwarranted fluid levels must sometimes be maintained to offset them; but where the handling of unconsolidated sands is not a problem of consequence and where water has been properly excluded, the principles developed here and the practices recommended should apply.

The principal objective of the producer should be to produce the maximum quantity of oil in the shortest possible time. Any method or equipment that will increase the rate of production during the early years of the life of the well, when gas pressure is high, will greatly augment the ultimate production. The maintenance of a proper fluid level in the well at all times will go far toward accomplishing this desired result.

For a given set of conditions surrounding the flow of oil into a particular well, in which the viscosity of the oil, the porosity and grain size of the sand, and the diameter of the well appear as constants, two variables determine the quantity of oil that will flow from the sand into the well. These are: the effective pressure behind or within the oil in the reservoir sand, and the fluid level maintained within the well. The former is the expulsive force that causes movement of oil from the sand into the well, while the latter determines the magnitude of a resisting force opposing such movement. The first of these factors is largely beyond the control of the oil producer, but it is in his interest to reduce the opposing force to the lowest economic limit.

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When oil is not being removed from a well and the opposing forces have had time to reach equilibrium, the height above the source rock to which the fluid rises in the well is an expression of the oil pressure; that is, the oil rises within the well above its source until the static pressure developed is equivalent to the pressure at which it enters. When this condition is reached, no additional oil will enter the well unless the pressure is sufficient to cause the fluid to overflow at the surface. If fluid is removed from the well, however, more will flow in until the former static head is again attained and equilibrium reestablished. If fluid is removed from the well at a constant rate, as in pumping, the fluid level will be permanently lowered by an amount sufficient to permit the necessary quantity to enter; and the amount of oil pumped from the well may be increased by maintaining a rate of production sufficient to reduce the fluid surface to some lower level. Eventually, by reducing the fluid level to successively lower levels, a rate of production is reached which is the maximum flow that the oil-bearing stratum is capable of yielding under the pressure prevailing in the productive sand.

Flow of oil from the sand into the well is due chiefly to the combined action of expanding natural gas and gravity. Gas pressure is unquestionably the controlling factor in determining the rate of oil production, particularly during the early life of an oil field when the gas pressure is high. Hydrocarbon gases dissolved in the oil under high pressure assume the gaseous phase when the pressure is reduced and expansion of this gas forces a part of the oil out of the sand into the well. Practically all the gas escapes from the oil during this process of expansion, but it is an inefficient process of expulsion in that a large percentage of the oil is normally left in the sands. During the later life of a well, the effect of gas pressure becomes comparatively insignificant; but gas pressure is never a wholly negligible factor, even toward the end of the product life of the well when gravity becomes the controlling factor. Gravity is, of course, always operative, but as it is usually a force of lesser magnitude than gas pressure, its effect is less apparent during the early stages of productivity when gas pressure is high.

As petroleum is expelled from the reservoir rock, the remaining oil will be concentrated in the lower portion of the sand stratum by the action of gravity, leaving the sand pores of the upper horizons comparatively open. This downward accumulation of residual oil leaves an open space above the main oil body through which gas may freely move. The gas is thus able to escape from the oil at points remote from the wells and move toward the well outlets without doing useful work in moving oil. When the gas pressure is high, the oil will rise to the cap rock in the immediate vicinity of the well, because of the elevated fluid level within the well during this period; this condition is illustrated in Fig. 1. When this stage is reached, it is probable that gas is effective in moving oil only

in the vicinity of the well, while areas remote from the well are drained chiefly by gravity.

It is apparent that if the fluid level within the well is maintained below the top of the oil sand, the gas will become still less effective, escaping freely into the well above the oil surface. Furthermore, the sands not in contact with oil show a tendency to dry out and accumulate troublesome solid hydrocarbons. Oil producers commonly recognize this principle and usually adjust their pump working barrels so that they "pump

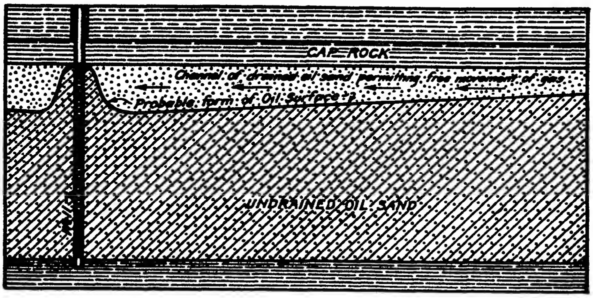

Fig. 1.—Drainage of gas through channel beneath cap rock from which oil has settled by gravity; well is assumed to be flowing.

off" or suck air when the fluid surface reaches the top of the oil sand. In so doing, however, when pressures are low, considerable oil production is sacrificed which might otherwise be realized through more effective gravity drainage. With the pump so placed, a fluid level somewhat above the top of the oil stratum must be maintained if the standing valve is to have adequate submergence.

To secure oil from wells by gravity drainage, the fluid surface within the well must be depressed below the top of the oil stratum; and the amount of oil flowing into the well as a result of gravity action will, within certain limits, increase as the fluid surface is reduced to lower levels. Slichter[1] has developed the following formula by means of which it is possible to compute the gravity flux to a well for any assumed position of the fluid level below the fluid surface in the productive sand:

$$f = \frac{2\,hka}{\log_e\left(1 + \frac{600}{r}\right)}$$

in which

f = flux to well, in cubic feet per minute
h = depth, in feet, to which fluid surface is lowered by pumping
k = a constant, which may be determined by experiment
a = thickness of productive stratum, in feet
r = radius of well, in feet

[1] C. S. Slichter: Theoretical Investigation of the Motion of Ground Waters. 19th. *Ann. Rept.*, U. S. Geol. Surv. (1897–98) part 2.

The 600 represents the assumed radius of drainage of the well, a figure commonly used for water wells. An appropriate drainage radius for oil wells would probably be somewhat less than 600 ft., but will vary with the gas pressure prevailing within the productive sand.

Inspection of this formula indicates that the production of the well is assumed to increase directly with the depression of the fluid level and that the maximum production may be expected when the fluid surface within the well is maintained at or near the bottom of the productive sand. King[2] finds, however, that this formula does not agree with results

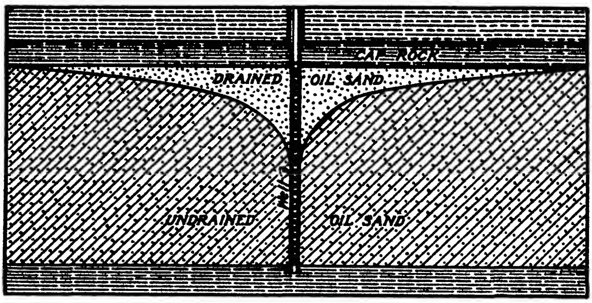

Fig. 2.—Depression of oil surface in vicinity of a pumping well in which fluid level is maintained below top of productive sand.

obtained in the pumping of water wells, the production actually obtained being less than the formula indicates, in some cases being only about one-half the theoretical amount.

A probable reason for this discrepancy between formula and practice may be found in the depression of fluid surfaces in the sand surrounding the wells, which in effect reduces the thickness of the productive stratum. As sketched in Fig. 2, the fluid surface in the vicinity of the well will eventually be depressed by continued pumping, the drainage slopes toward the well assuming the form of a sharply flexured, inverted, conical surface. All oil entering the well must flow through the cylindrical walls below the fluid surface. As the fluid level within the well subsides, the wall area exposed to the oil decreases; and as, for a given rate of production, the resistance to flow increases as the wall area decreases, the production must decline when the wall area becomes so constricted as to impede seriously the flow of oil. In other words, increased gravity flow and increased wall resistance, both resulting from depression of the fluid level, are opposing factors and the maximum rate of production is realized only when a proper balance is secured between them.

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[2] F. H. King: Principles and Conditions of the Movements of Ground Water. U. S. Geol. Surv. 19th *Ann. Rept.*, (1897–98) part 2.

A formula[3] expressing the relation between pressure, quantity of oil produced, and thickness of the productive sand that is derived from Slichter's data, is as follows:

$$P = C \log_{10} \frac{L}{r} \frac{Qu}{td^2o^{3.4}}$$

in which

P = pressure loss, in feet of water, in moving oil into well
C = a constant;
Q = quantity of oil produced, in barrels per day
d = effective diameter of sand grains, in millimeters
u = viscosity of the oil, in poises
o = percentage porosity
t = thickness of productive sand, in feet
L = drainage radius of well, in feet
r = radius of well, in feet

In this formula, for a particular well at a given time C, d, u, o, L, and r will be constants; hence,

$$P \propto \frac{Q}{t}, \text{ or } Q \propto Pt.$$

With the aid of this latter expression, the variation in productivity of a well producing from an oil sand 100 ft. thick has been computed for different assumed oil pressures; Table 1 gives the results. In computing the results indicated in each column of the table, it is assumed that the oil enters with a gas pressure equivalent to that designated at the head of the column. The amount of additional gravity pressure resulting from successive reductions of the fluid level below the top of the productive sand is then determined and the flow computed for each pressure increment, full account being taken of the accompanying decrease in the effective thickness of the productive sand. Fig. 3 shows graphically the results of one series of computations and indicates the method of computation. In these calculations, it is assumed that 5 ft. of oil head creates a static pressure of 2 lb. per sq. in. It is probable that the figures represented in the last few lines of the table could not be realized practically, it being impossible to depress the fluid surface in the sands immediately surrounding the well to the bottom of the productive stratum while the gas pressure is high. If this could be done, theoretically there would be no production, as indicated in the table.

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[3] Increasing the Production of Petroleum by Increasing the Diameter of Wells; this volume, p. 1276.

The data of Table 1 and the formula from which they are derived, lead to the following conclusions:

1. When the static fluid level[4] in the well is at an elevation above the top of the source rock greater than the thickness of the productive sand,

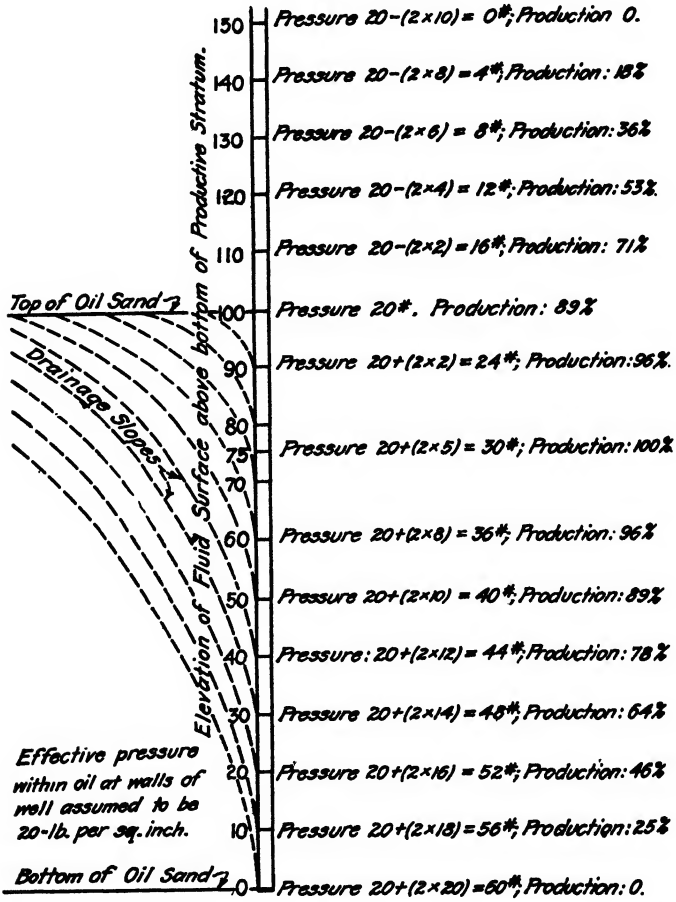

FIG. 3.—VARIATION IN PRODUCTION FOR DIFFERENT POSITIONS OF FLUID LEVEL IN A WELL.

the operating fluid level[5] giving maximum production is always at the top of the productive sand.

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[4] By "static fluid level" is meant the fluid level attained after a period in which on oil is pumped and forces have had time to come into equilibrium.

[5] By "operating fluid level" is meant the stationary position of the fluid surface after prolonged pumping at a uniform rate.

Table 1.—*Percentage of Production Obtained from Sand 100 Ft. Thick, for Different Positions of Fluid Level and with Different Effective Pressures*

Elevation of Fluid Level above Bottom of Sand, Feet	Effective Pressure at Walls of Well, Pounds							
	0	5	10	20	30	40	50	100
	Percentage of Maximum Possible Production							
100	0	39	64	89	98	100	100	100
95	19	53	73	93	99	99	99	97
90	36	64	81	96	99	99	97	94
85	51	74	87	98	99	98	95	90
80	64	80	92	99	99	96	93	86
75	75	88	96	100	98	94	90	82
70	84	94	98	99	96	91	87	78
65	91	98	99	98	93	86	83	74
60	96	99	99	96	90	84	79	70
55	99	99	98	93	86	79	75	65
50	100	99	96	89	82	75	70	60
45	99	96	92	84	76	69	65	55
40	96	92	87	78	71	64	59	50
35	91	84	81	71	64	58	53	44
30	84	78	73	64	56	51	47	38
25	75	69	64	55	49	44	40	32
20	64	58	54	46	45	38	33	26
15	51	46	42	36	31	28	25	20
10	36	32	30	25	21	19	17	14
5	19	17	15	12	11	10	9	7
0	0	0	0	0	0	0	0	0

2. When the static fluid level is less than double the thickness of the productive sand above the bottom of the source rock, for maximum production the operating fluid level must be maintained at an elevation above the bottom of the productive sand equivalent to half that of the static fluid level above the same point.

3. For best results, the operating fluid level must never fall below the middle of the productive stratum.

Importance of Knowledge of Operating Fluid Level in Securing Maximum Production

The foregoing analysis should convince the reader that the maximum production of oil from a well is realized only when the fluid surface within the well is maintained at a definite level. Furthermore, some of the factors that determine this fluid level are variable; therefore the critical fluid level itself is variable. That is, a position of the fluid level that is

proper at one period in the life of a well, is improper at some later period when pressures are lower or when the radius of drainage of the well is smaller. In general, these two variables are progressively reduced throughout the life of the well, so that the fluid level should be correspondingly lowered; but there is no uniformity in this variation in different wells, for local differences in texture and thickness of the oil sand and variation in the properties of the oil are important variables in comparing the results obtained from wells in different localities. Again, when back pressure is applied to a well to conserve gas or to control sand influx, the fluid level within the well will be depressed; or if vacuum is applied, the fluid level will rise. In such cases, slight variation in the pressure conditions within the well will necessitate prompt change in the pumping adjustments if efficiency in oil extraction is to be maintained.

In addition to increasing the current and ultimate recovery of oil, maintenance of the most efficient fluid level in a pumping well will probably also result in maximum economy in the expulsive force of the occluded and dissolved natural gas. It is well known that many wells that are capable of flowing 40 or 50 bbl. of oil per day will often produce double that amount when pumped.

While the importance of maintaining a proper fluid level in pumping wells is generally recognized among oil producers, few appear to have developed any definite method of determining the position for the oil surface that will yield maximum production, other than by "cut-and-try" methods. Usually, when a well is placed "on the beam," the working barrel is lowered successively to lower and lower positions and different lengths of stroke or pumping speeds are experimented with until the combination giving the maximum production is found. Often during such tests, the results are influenced by other variables such as gas flows, temporary mechanical inefficiency of the pump due to sand incursion, gas locks, etc., and the operator in many cases adopts a system of pumping that does not result in the maximum production of oil. Too frequently, he assumes that the pumping adjustments determined as suitable during the early life of the well are proper at later periods; that is, he fails to recognize the importance of changing conditions which require a change in fluid level if maximum production is to be maintained. Few operators have any knowledge of the operating submergence of their pumps, figures on submergence of working barrels usually representing the static submergence or the depth below the fluid surface after the pump has been idle for a time and the oil has had time to rise in the well until partial or complete equilibrium of forces has been reached.

A Fluid-level Indicator for Use in Oil Wells

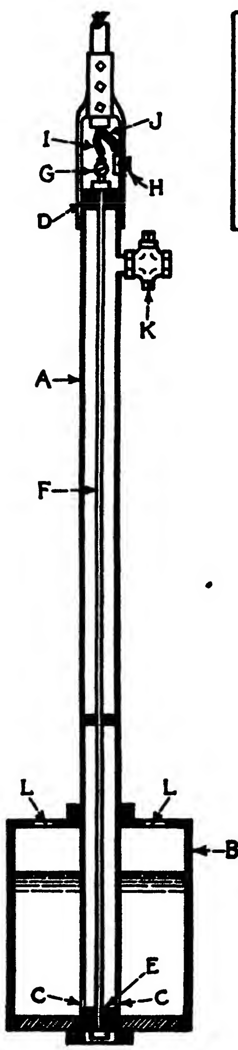
With the purpose of providing a means of continuously recording the operating submergence of an oil well pump, or the position of the fluid

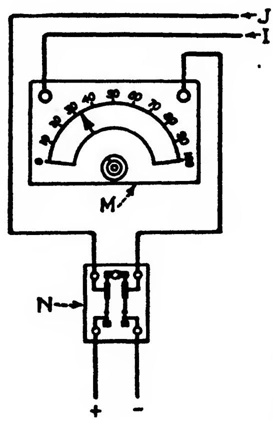
level within the well while the pump is at work, the writer has devised a fluid-level indicator, the use of which should lead to a better understanding of the conditions within the well and to greater efficiency in oil extraction. This indicator is shown in Fig. 4 in its simplest form. A tube *A* is attached rigidly to a cylindrical cup *B* and is concentric therewith; these parts must be made of iron, steel, or some other metal that conducts electricity but is not attacked by mercury. The cup *B* is partly filled with mercury, which finds access to the interior of tube *A* through holes *C* near its lower end. Both ends of the tube *A* are tightly sealed with suitable plugs *D* and *E* made of material that is not a conductor of electricity, so that the space within the tube is capable of retaining air and mercury under pressure without leakage. Extending through the center of the tube *A*, and stretched rigidly between the insulating plugs *D* and *E*, is a wire *F* made of high electrical resistance metal, such as nichrome. Electrical connections *G* and *H* are provided near the top of tube *A* by means of which wires *I* and *J*, made of copper or other material of low electrical resistance, are connected respectively with the high-resistance wire *F* and the tube *A*. Wires *I* and *J* are covered with insulating material and twisted together to form a cable that extends to the surface and to the instrument where the fluid level is to be recorded. This cable is sheathed in a covering that will protect the insulating material about the wires from detrimental contact with the fluid in which it is to be immersed. The cable is attached to a supporting bail screwed to the top of tube *A* and serves as a suspending medium by means of which the entire device may be lowered to the bottom of the well.

Before lowering the indicator into working position, valve *K*, which provides a means of adjusting the volume of air above the mercury surface in the tube, is opened, thereby causing the mercury to assume the same level in tube *A* as that of the main body of mercury in cup *B*; the valve is then closed. As the device is lowered into the well fluid, the latter has access to the top surface of the mercury in the cup *B* through holes *L* in the cover; the mercury surface in the cup is depressed as the static head increases, while air imprisoned in the upper part of the tube is compressed to an equivalent pressure and correspondingly smaller volume. The greater the static head imposed above the mercury surface, the more the latter will be depressed in the cup *B* and elevated in the tube *A*; that is, the greater the fluid pressure, the shorter will be the length of resistance wire exposed above the mercury surface.

Near the point where the fluid level is to be recorded, wires *I* and *J* are connected with a source of electricity of suitable voltage, through an ammeter *M* sufficiently sensitive to indicate small changes in the flow of current; see Fig. 5. The source of the electric current may be a lighting circuit with a low-voltage transformer in circuit or, if the well is not too deep and a milliammeter is available, a group of dry cells connected in

series or a storage battery may be used. The voltage must be proportioned to the resistance imposed by the circuit and the high-resistance wire *F* must be of such length and cross-section as will make the ammeter





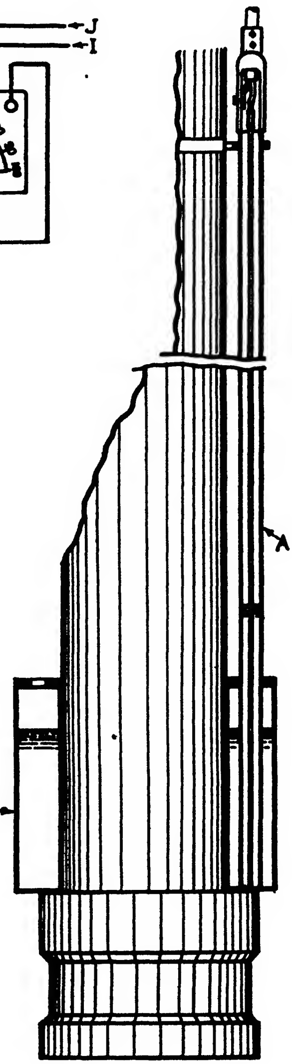


FIG. 4. FIG. 5. FIG. 6.

FIG. 4.—VERTICAL SECTION THROUGH CYLINDRICAL TYPE OF FLUID-LEVEL INDICATOR.
FIG. 5.—AMMETER AND CONNECTIONS FOR USE WITH FLUID-LEVEL INDICATOR.
FIG. 6.—ANNULAR FORM OF FLUID-LEVEL INDICATOR FOR USE WITH PLUNGER PUMP.

sensitive to small changes in the position of the mercury surface. If greater length is needed for this high-resistance wire than is afforded by the length of tube *A*, the resistance element may be in the form of a spiral

wound on a core of some non-conducting material. For very low submergence, the space within the tube above the mercury surface may be maintained under vacuum as in the ordinary mercury barometer.

The electric current flowing into the device through wire J, is short-circuited from the walls of tube A, through the mercury to the resistance wire thence back to the ammeter through wire I; hence, as the mercury surface rises in tube A, as a result of increase in the superimposed fluid head, the current flows through a shorter length of the resistance wire, resulting in more current passing through the ammeter. By calibrating the ammeter dial to accord with computed changes in the volume of air imprisoned in tube A, or of the mercury surface in A, in terms of the known or measured resistance offered by the circuit for different positions of the mercury surface, a direct reading of the depth of superimposed fluid is obtained. For use under low submergence, a brine solution or a solution of any electrolyte may be used instead of mercury. By using a recording type of ammeter, a continuous record is secured. Unless a continuous record is desired, however, the current need be used only at such times as measurements are required, switch N providing an ever-ready means of controlling the current.

The writer has constructed an indicator of the type described, having an iron tube 0.824 in. in internal diameter and 2 ft. 8 in. long, which is sensitive to a change of as little as 1 ft. in the position of the fluid level. The high-resistance element is a straight length of No. 22 "nichrome" wire (resistance about 1 ohm per foot) and No. 6 copper wire (resistance 2.1 ohms per mile) is used for the electric circuit. This instrument has been tested for the measurement of fluid depths as great as 150 ft., using a storage battery having a potential of 5.6 volts as a source of current.

If a lighting circuit furnishes the current, the size of the resistance wire must be proportioned so that the resistance element does not become heated. At elevated temperatures, the resistivity of the circuit will be much decreased, the pressure of the imprisoned air above the mercury will be increased, and the mercury will be partially vaporized.

For use in connection with an oil-well plunger pump, the design may be slightly altered, as illustrated in Fig. 6. Here the cup B has been replaced by an annular mercury reservoir, the inner wall of which fits snugly about the outside of the pump working barrel, resting upon the upper edge of the foot piece. The tube A attached to the mercury reservoir, as before, extends upward in close contact with the outer surface of the pump working barrel and is attached thereto near its upper end. The cable containing the copper conductors is bound, at intervals, to the outside of the well tubing to prevent its becoming entangled as the latter is inserted or withdrawn from the well.

Use of Fluid-level Indicator in Determining Proper Rate of Pumping to Secure Maximum Production of Oil

Assuming that a fluid-level indicator has been installed at a pumping well and has been properly adjusted to indicate the approximate position of the fluid surface in the well at all times, it should be possible to determine quickly the length of pumping stroke and frequency of stroke that will yield a maximum production of oil.

If the pump is started after a period of idleness, the fluid level will be high: probably high enough to have reached its static level, or position of equilibrium, with the oil pressure at the horizon where it enters the well. The working barrel should be placed as near the bottom of the productive stratum as is consistent with proper exclusion of sand from the pump. A suitable length of stroke (according to the depth of the well and its probable production) should be provided by proper adjustment of the wristpin in the crank. The engine or motor is then started, using at first, say, 15 strokes per minute, and the fluid-level indicator observed until equilibrium is reached between the incoming oil and that pumped out. When the fluid level becomes stationary, the rate at which the oil is discharged from the lead line is carefully gaged.

If the fluid level is higher than that at which computations (similar to those described in the foregoing pages) indicate the maximum production should be secured, the speed of the engine is increased until a lower fluid level is established and a second gaging test is made. This process is repeated until the frequency of stroke and operating fluid level giving maximum productivity is determined. The fluid level must reach a position of equilibrium in each test and the fluid level adopted for permanent adjustment of the pumping speed must be that which yields the maximum quantity of oil. If oil is pumped from the well more rapidly than it is able to enter, continued sinking of the fluid below the depth at which proper action of the pump is secured will at once be apparent. This adjustment can be made as satisfactorily, perhaps, without the aid of a fluid-level indicator or without any knowledge of the position of the fluid surface, but the indicator will make it possible to determine the proper pumping speed with greater precision and more expeditiously.

While the fluid-level indicator will be of considerable aid in making the initial adjustments, its chief value is found in the later period of routine operation. If wear of the pumping device or sand accumulation or a "gas lock" in the working barrel has occasioned mechanical inefficiency resulting in decreased production or if, for any reason, the flow of oil into the well has increased, the fluid-level indicator will show a higher level than that determined as most efficient, and proper remedial measures may be taken or the pumping speed increased until the proper level is again established. Again, if the yield of the productive sand should

suddenly decrease, as in the case of clogging of the sand pores with paraffin, the fluid-level indicator will prescribe a slower rate of pumping. By frequent inspection of the fluid-level indicator, the operator is able promptly to adjust the pump to meet any contingency, and continued gaging tests of individual wells become unnecessary in so far as pump adjustments are concerned. Maximum efficiency in oil production may thus be secured.

By a little ingenuity in the arrangement of electrical circuits connected with the ammeter or indicator circuit, an electric bell could be caused to ring in some central establishment on the lease whenever the fluid level in any well deviated from its pre-established position, thus indicating breakage of rods, parting of tubing, "sanding up" of the pump, failure of the power, or other irregularities resulting in deviation from normal operating conditions. It should even be possible, by suitable electrical connections, to cause the fluid-level indicator to increase or decrease automatically the speed of the engine or motor when variation in fluid level requires such adjustment.

Use of Fluid-level Indicator in Determining Source of Water in Oil Wells

A knowledge of fluid levels in oil wells is important in other ways; for example, if water breaks into a well from an extraneous source, it may be difficult to determine the horizon from which it comes; yet a knowledge of the source of the water is essential before repairs can be undertaken. If the well is equipped with a pump and a fluid-level indicator and the amount of fluid entering the well is within the capacity of the pump, determination of the horizon at which the water enters becomes a simple matter. All that is necessary is to permit the water to accumulate in the well until it establishes a head at which no more water enters. The pump is then started, first at low speed and then at successively higher speeds until the lowest possible stationary operating fluid level is reached; this will be approximately the level at which water enters. When the speed is increased beyond that necessary to maintain this lowest stationary fluid level, the water is being removed more rapidly than it enters the well and the fluid level will continually subside.

Summary and Conclusions

The position of the fluid surface maintained within a well has an important influence on its productivity. Under the conditions prevailing within a well at a given time, maximum production is realized only when the fluid surface is maintained at a particular level and slight variation from this economic fluid level will often greatly alter the

recovery. If the static fluid level and the thickness of the productive stratum are known, the elevation at which the fluid surface should be maintained may be approximately computed. For low pressures, a lower level will be preferable; never, however, below the middle point of the productive sand.

The importance of a knowledge of the fluid levels maintained in wells while the pumps are at work is emphasized. To provide a means of determining the level of the fluid surface within a well at all times, a design for a fluid-level indicator is described and the advantages accruing to the oil producer through its practical use are discussed. The use of such a device should lead to a greater rate of production and consequently greater ultimate production; it will also be useful in indicating promptly breakage or mechanical inefficiencies of the pumping equipment. Its possible use in locating the source of water entering an oil well from an extraneous source is also suggested.

Determining the Constants of Oil-production Decline Curves*

BY HARRY M. ROESER,† WASHINGTON, D. C.

(New York Meeting, February, 1925)

As a result of the publication, several years ago, of some articles on determining the constants of empirical formulas, the determining the constants of types of curves used for estimating the production decline of oil wells was brought to the writer for study. Methods requiring the minimum of time and labor and the maximum of rigor were sought, as it appeared that the nature of the data from which such curves are computed and the relative uncertainty of occurrence of the events predicted from them did not justify close adherence to the theory on which the solution of such problems is ordinarily based.

The technical deficiencies of the solutions presented in this paper, from the standpoint of the method of least squares, are readily apparent to those familiar with that method, but their presentation in detail here is irrelevant to the subject matter. However, it is the author's conviction, after a rather exhaustive study of the problem, that the value of the solutions lose little by the approximate application of the conventional theory.

It must be understood by those who use these formulas that the solutions herein given, and the formulas based on them, are merely facilities to aid the valuation engineer in forecasting future events. It is assumed, also, that before application is made of them, prescient judgment based on the circumstances in each case, shows that the forecast has some probability of realization. On this basis only will these formulas be found useful.

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Engineers in the oil industry have settled upon two types of curves for estimating production decline, *viz.*, $y = kr^x$, and $y = kx^n$ wherein y is the production, in barrels, for a given accounting period x, and k, r, and n are constants. Given the constants, the formulas can be used to determine the production for a subsequent period and the total available oil under ground after a given period. Numerical examples on which to demonstrate the proposed solutions may be found in the article by Charles S. Larkey, in MINING AND METALLURGY.[1] They have been selected because the results herein obtained may be directly compared with the results obtained by methods more or less current in the industry. In fact, this paper may be considered as supplementing that article.

SOLUTION FOR FORM $y = kr^x$

By taking the logarithms of both sides of the equation $y = kr^x$, the form will plot as a straight line on semi-logarithmic cross-section paper. Thus, $y = kr^x = \log y = \log k + x \log r$.

Plotted on semi-logarithmic cross-section paper, this has the y-intercept k, and slope r. Exactly similar results may be obtained by plotting values of log y against values of k on ordinary cross-section paper.

It has been shown[2] that the best straight line that can be fitted to a set of observations distributed according to the law $y = a + bx$ must pass through the point $x, y = x_m, y_m$, where x_m is the arithmetic mean of the observed values of x, and y_m is the arithmetic mean of the observed values of y. This fact may be made extremely useful in any problem requiring the fitting, by trial, of a straight line to a set of observations presumed to follow a linear law with respect to the independent variable because one point through which the required line must pass is rigorously determined. Consider for example the observations given in Fig. 2 of the article by Mr. Larkey.

x Years	y Barrels	Log y
1	36,952	4.56763
2	31,753	4.50178
3	23,153	4.36461
4	20,834	4.31877
5	17,514	4.24339
6	13,041	4.11531

Mean value of $x = x_m = 3.5$; mean value of $\log y = y_m = 4.35192$.

According to the theorem, the best straight line through the plotted points must pass through the point $x_m, y_m = (3.5, 4.35192)$, and may be located by rotating a straight-edge about that point until it appears to be in the proper position. Those who cannot rely on their judgment to decide the best position may resort to the following expedient:

[1] (July, 1923) **4**, 341; it is reprinted in this volume, see p. 1322.

[2] *Phys. Rev.* (1917), **9**, 80.

Consider any two observation equations

$$\log y_1 = \log k + x_1 \log r \tag{1}$$

and

$$\log y_2 = \log k + x_2 \log r \tag{2}$$

Subtract (2) from (1)

$$\log y_1 - \log y_2 = (x_1 - x_2) \log r,$$

or,

$$\log r = -\frac{\log y_1 - \log y_2}{x_2 - x_1}$$

This gives an approximation for log r that is the slope of the required line. The value of log r from a single calculation such as this should not be considered the correct value; the mean of a sufficient number to give a stable value should be taken. There are as many such calculations for log r possible as there are combinations of the number of observations two at a time; in the case at hand, there are fifteen possible, and if the fifteen are made, the mean of the group should be exactly the same as that calculated by the method of least squares shown in Mr. Larkey's article. For practical purposes, only enough need be made to satisfy the computer that he has a stable value.

Having determined log r, and consequently r, k may be determined from the relation,

$$\log k = y_m - x_m \log r,$$

wherein y_m and x_m are as defined before. The curve is thus completely determined.

SOLUTION FOR FORM $y = kx^n$

If the center of coördinates of the original data is properly located, the equation $y = kx^n$ plots as a straight line on logarithmic cross-section paper; but unless so located, it will plot as a curve concave toward the y axis, if the center of coördinates is too far to the left, and convex, if too far to the right. This fact is emphasized on p. 78 of the Manual of the Oil and Gas Industry, issued by the U. S. Internal Revenue Service, and in Mr. Larkey's article. A disadvantage of the equation in the form given is that two independent computers will obtain the same constants, and thus the same curve, only by chance except through laborious calculation. The curve type, as adopted, is fundamentally inadequate; the difficulty would be eliminated if the following form were used;

$$y = k(x + c)^n$$

in which k, c and n are constants. With this form, any two independent computers who determine the constants by ordinarily reliable methods must necessarily derive the same curve. Further, the curve as determined will plot as a straight line on logarithmic cross-section paper. A short solution for the constants k, c, and n will be illustrated by determining them for the curve shown in Fig. 4 of Mr. Larkey's article.

Take the logarithm of both sides of this equation and there results $\log y = \log k + n \log (x + c)$. Treating any two observation equations thus, we have

$$\log y_1 = \log k + n \log (x_1 + c) \tag{1}$$
$$\log y_2 = \log k + n \log (x_2 + c) \tag{2}$$

Subtracting (2) from (1) and solving for n,

$$n = \frac{\log y_1 - \log y_2}{\log (x_1 + c) - \log (x_2 + c)} \tag{3}$$

For convenience in handling solutions of this type, let it always be considered that the value of $(x + c)$ corresponding to the first observational value of y is unity.

The constant c and the corresponding value of n may be determined by adding different trial values of c to values of x and solving equation (3) for n. The value of c that gives a constant value of n for all pairs of observations x_1, y_1 and x_2, y_2 is the proper value of c and the value of n thus found is the one required. A simple and systematic manner of doing this is as follows:

Decline Data for Property in Sec. 12, T. 21N., R. 12E., Tulsa County, Okla. (*Larkey's Article*)

y	Log y	First Differences (Log y_1 − Log y_2)	$(x + c)$ Years	Log $x + c$	First Differences Log$(x_1 + c)$ − Log$(x_2 + c)$
20,567	4.31317		1	0.00000	
		+0.14956			−0.30103
14,575	4.16361		2	0.30103	
		+0.12261			−0.17609
10,990	4.04100		3	0.47712	
		+0.10802			−0.12494
8,570	3.93298		4	0.60206	
		+0.09193			−0.09691
6,935	3.84105		5	0.69897	
		+0.08221			−0.07918
5,739	3.75884		6	0.77815	
					−0.06695
			7	0.84510	
					−0.05799
			8	0.90309	
					−0.05115
			9	0.95424	
					−0.04576
			10	1.00000	
					−0.04139
			11	1.04139	
					−0.03779
			12	1.07918	

Having prepared a table of logarithmic differences and assuming that c is a certain integral value, divide the succeeding differences for log y in order by the differences for the appropriate values of log $(x + c)$.

Thus assuming that $c = 2$, then $(x_1 + c) = 3$ and the log $(x + c)$ difference corresponding to $(x_1 + c) = 3$ is -0.12494. Dividing the first log y difference $(+0.14956)$ by this quantity yields the value $n = -1.197$. In successive order, $0.12261 \div -0.09691 = -1.265 = n$. This variation in the two values of n is too great to support the possibility of 2 being the correct value for c, so that it can be dropped and the same procedure may be carried out for $c = 3$, or until a value is found that yields a reasonably constant value of n in the successive divisions. The divisions may be made with sufficient accuracy on a slide rule. The accompanying table is not necessary to the practical solution but it illustrates how the values of n vary corresponding to assumed values of c.

VALUES OF n CORRESPONDING TO ASSUMED VALUES OF c

$c = 0$ n	$c = 1$ n	$c = 2$ n	$c = 3$ n	$c = 4$ n	$c = 5$ n	x_2	x_1
−0.497	−0.849	−1.197	−1.543	−1.889	−2.234	2	1
−0.696	−0.981	−1.265	−1.548	−1.831	−2.114	3	2
−0.864	−1.115	−1.364	−1.613	−1.863	−2.111	4	3
−0.949	−1.161	−1.373	−1.585	−1.797	−2.009	5	4
−1.038	−1.228	−1.418	−1.607	−1.797	−1.986	6	5
			Mean =	−1.835			

The values in each column of the table are computed, as outlined, for each assumed value of c from $c = 0$ to $c = 5$. It will be noted that in all the columns corresponding to $c = 3$ or less the values of n tend to become greater as x increases. For values of $c = 4$ or greater the corresponding values of n become less as x increases. This indicates that the correct value of c lies between 3 and 4; but as integral values are satisfactory tabular interpolation need not be applied to determine the fractional value and $c = 4$ may be selected as the correct one. The mean of the five values of n may be taken as the proper value of n; or if a better one is desired, after having selected the value of c more values of n may be computed and the mean of the group taken. With the set of observations at hand, fifteen such solutions are possible and the mean value of n from all should agree exactly with Mr. Larkey's solution.

The mean of the five values, in the accompanying table, for $c = 4$ is $n = 1.835$. This is a practical agreement with Mr. Larkey's solution,

which results in beginning his values of x with $x = 5$, and $n = 1.8415$. The values of n and c thus determined establish the plot as a straight line on logarithmic cross-section paper or on ordinary cross-section paper if values of log y are plotted against values of log $(x + c)$. It is known from the theorem cited above that if y_m is the mean of the values of log y and x_m is the mean of the values of log $(x + c)$ the line must pass through the point $(x_m, y_m) = (0.86326, 4.00844)$. The value of n determines the slope and thus the line is determined.

The constant k is determined from

$$\log k = y_m - nx_m = 4.00844 + 1.835 \times 0.86326 = 5.59252$$

$k = 391{,}300$, which determines the curve.

Estimation of Available Underground Oil Supply

The extreme extrapolation required when estimating the available underground oil supply after the production-decline curve for a well or field has been determined would be discountenanced in ordinary physics or engineering practice. Granting, however, that the exigencies of the situation justify it in this case, simpler methods may be employed for estimating the underground supply than have come to the author's attention.

To use the formula $y = kr^x$, the total oil remaining underground after a given period x' may be computed from the formula,

$$Q = \frac{kr^{x'}}{\log_e r} = kr^{x'}\log_e\left(\frac{1}{r}\right)$$

This formula is derived by integrating function (1) from x' to infinity. If x'' be the time at which the economical production limit will be reached, the total obtainable supply is

$$Q = \frac{k}{\log_e r}(r^{x''} - r^{x'})$$

which is derived by integrating function (1) from x' to x'', x'' being determined from

$$x'' = \frac{\log y' - \log k}{\log_e r}$$

in which y' is the economical production limit.

Similarly for the form $y = k(x + c)^n$. The total oil remaining underground after a given period x' is,

$$Q = \frac{k(x + c)^{n+1}}{n + 1}$$

and the total obtainable supply is

$$\hat{c} - \frac{k}{n+1}\left[(x'' + c)^{n+1} - (x' + c)^{n+1}\right]$$

in which x'' is the time at which the economical production limit will be reached and is determined from

$$\log\ (x'' + c) = \frac{\log y' - \log k}{n}$$

y' being the economical production limit.

Mathematical Determination of Production Decline Curves*

By Charles S. Larkey

Numerous papers have been published on the use of graphic methods for determining the best curve for estimating the production decline of oil wells but, as far as the writer has been able to ascertain, nothing has been published showing how curves may be worked out mathematically that will conform most closely to the production data under consideration in any given instance; hence the writer has endeavored to show just how such application can be made.

Among the valuation engineers, two types of curves are in current use for the representation of the decline in production of oil wells. One may be represented by the equation, $y = kr^x$; this is sometimes known as a percentage curve, for the production for any period is multiplied by a constant rate or percentage to obtain the production for the succeeding period. It appears as a straight line on semilogarithmic cross-section paper. The other curve may be represented by the equation, $y = kx^n$, and is shown as a straight line on logarithmic cross-section paper.

In each equation, y represents the number of barrels produced in a given period of time, and x the successive periods of time. The other letters are constants to be determined for each well, or group of wells considered in arriving at the most probable curve to represent the rate of production for a given property. From this the underground reserves may be estimated by extrapolation, or by extending the curve beyond the last known period of production to show the most probable production values for the future.

Application to the Burbank Pool

Fig. 1 relates to a property in the Burbank Pool, Osage County, Okla. The production is shown as an average per well per month, is plotted to the vertical scale of barrels on the left-hand margin and to the horizontal scale of months at the bottom of the chart. In column y, the number of barrels is listed beginning with May, 1922, as the first month on which to base a decline curve. The type of curve used is of the form, $y = kr^x$, or, expressed in logarithms, $\log y = \log k + x \log r$, in which $\log k$ and $\log r$ are constants to be determined so that the curve will most closely approximate the production data given.

* Presented before the Mid-Continent Section, Tulsa, Okla., Apr. 27, 1923.

To determine the best values to be assigned these constants, the work may be tabulated as shown in Fig. 1, in which, for convenience, log k is represented by b and log r by m, the equation becoming $\log y = mx + b$.

Substituting the successive values of x and log y in this equation, a series of equations are formed in which m and b are unknowns. Thus, writing the unknowns in the first member and log y in the second member, the first equation, by substitution, becomes

$$b + m = 4.1427$$

the second, $$b + 2m = 3.9608$$

the third, $$b + 3m = 3.9374$$

and so on, one equation being formed for each set of values in x and y.

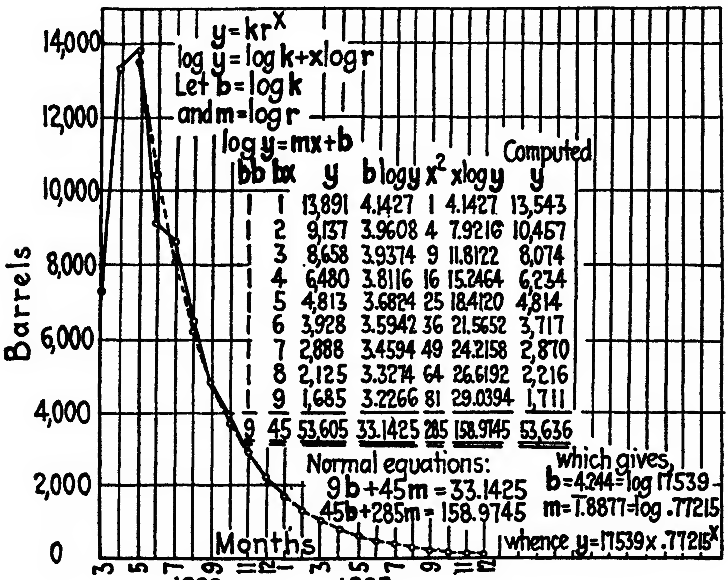

Fig. 1.—Property in Burbank pool.

From any two of these equations thus formed, b and m may be determined directly by means of the familiar algebraic principles of simultaneous equations; but if different pairs of equations are taken, different values for b and m will be given in each instance; hence, to obtain values that will most nearly satisfy the conditions of all the equations in the series, it is necessary to adopt some plan whereby each equation is given an equal weight. This is done by multiplying each equation, in turn, by the coefficient of b in such equation, and adding all the resulting equations together to form a normal equation. Then, in the same manner, each

equation is multiplied in turn by the coefficient of m in such equation and the resulting equations added together to form a second normal equation.

In Fig. 1, under the columns headed bb, bx, and $b \log y$, are to be found the resulting coefficients of the series when multiplied by the coefficient of b, which is 1 for each equation and does not change the value of the original coefficients. The sums of these columns give the coefficients for the first normal equation, $9b + 45\ m = 33.1425$.

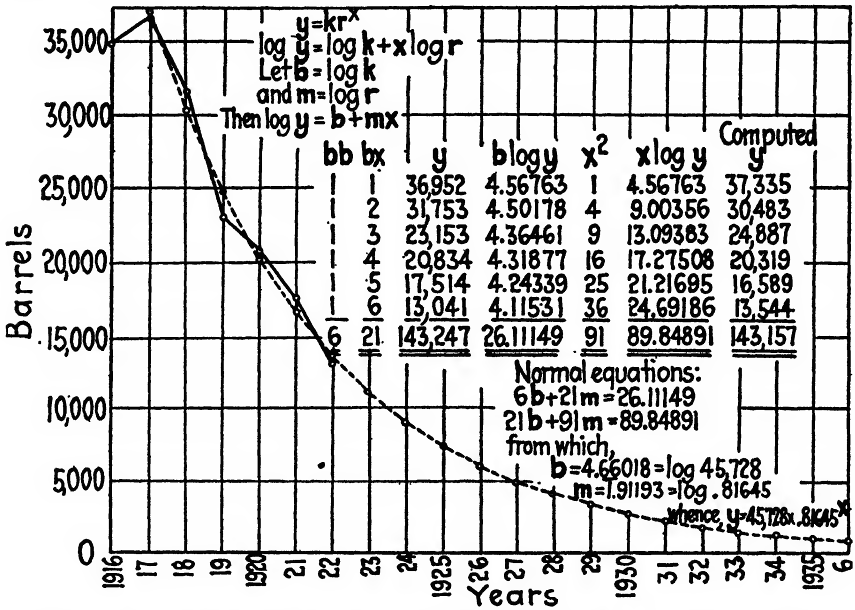

FIG. 2.—PROPERTY IN SEC. 33, T. 18N., R. 7E., CREEK COUNTY, OKLA.

The columns headed bx, x^2 and $x \log y$, show the resulting coefficients when each equation is multiplied by the coefficient of m, which is the value given for x. The sums of these columns give the coefficients for the second normal equation, $45b + 285m = 158.9745$. Solving for b and m in these two equations

$$b = 4.244 \quad = \log 17.539$$
$$m = 1.8877 = \log 0.77215$$

Substituting these values for the constants in the original equation, the curve is represented by $y = 17.539 \times 0.77215^x$. This curve is shown as a dotted line on Fig. 1 and approximates the production curve very closely.

The mathematical proof that it is the most probable curve, of the type selected, to represent the given data, will not be given here as this is fully treated in a number of excellent works on the method of least squares, of which method this is merely an application to a particular type of equation.

Fig. 2 shows the application of the same type of equation to the production of a property in the Cushing Pool, Creek County, Okla., the constants being arrived at in the same manner as before. In this example the production periods are years instead of months and the production has not been reduced to an average per well, as the same number of wells were producing throughout that portion of the life of the lease considered. If, however, it is desired to express the equation as an average per well it is only necessary to divide the constant, 45,728, shown in the final equation, by the number of wells actually producing.

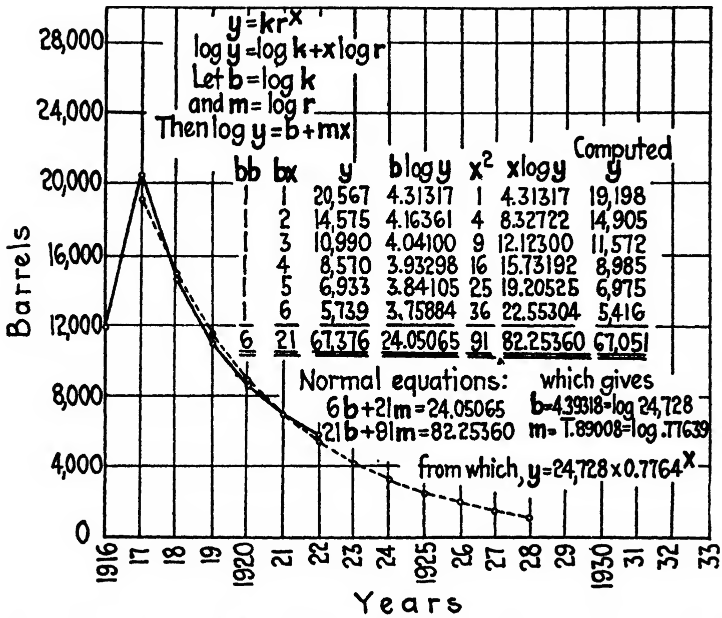

FIG. 3.—PROPERTY IN SEC. 12, T. 21N., R. 12 E., TULSA COUNTY, OKLA.

APPLICATION TO TULSA COUNTY, OKLA.

In applying the same type of equation to a property in Sec. 12, T. 21N., R. 12E., Tulsa County, Okla., it was found, as shown in Fig. 3, that the theoretical curve did not follow the production curve very closely. Here clearly an equation of the type $y = kr^x$ does not apply, and a curve of the type $y = kx^n$ is used. This application is shown in Fig. 4. Expressing the equation in the logarithmic form,

$$\log y = \log k + n \log x,$$

in which $\log k$ and n are constants to be determined. The method of determining these constants is essentially the same as that used in the other type of equation, the principal difference being that x must

be assigned some initial value such that when plotted on logarithmic cross-section paper the points will approximate a straight line. This was actually done in this instance by plotting on the logarithmic paper and shifting the points to right or left until such alignment was apparent. This gave an initial value of 5 for x, the successive values of x being in arithmetic sequence. These values are used in the table shown on Fig. 4. In this table, $u = \log y$; $b = \log k$; and $m = \log x$. The coefficients

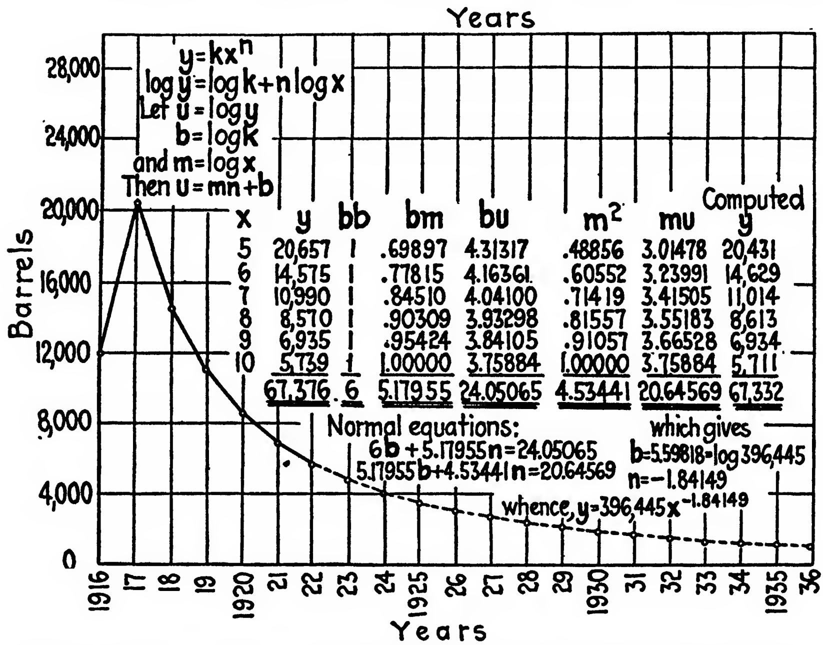

FIG. 4.—PROPERTY IN SEC. 12, T. 21N., R. 12E., TULSA COUNTY, OKLA.

for the first normal equation are obtained from the sums of the columns headed bb, bm, and bu, which represent a series of equations multiplied by the coefficients of the first unknown b, giving the equation $6b + 5.17955n = 24.05065$.

The coefficients for the second normal equation are obtained in a similar manner from the columns headed bm, m^2 and mu, which represent the same series of equations multiplied by the coefficients of n, giving the equation $5.17955b + 4.53441n = 20.64569$.
Solving these equations it is found that

$$b = 5.59818 = \log 396{,}445$$
$$n = -1.84149.$$

Substituting these values in the type equation,

$$y = 396{,}445x.^{-1.84149}$$

The curve of this equation is shown as a dotted line on Fig. 4, where it appears only in extension of the given production curve, for the reason that the computed and the actual values of y are so nearly the same that the two curves almost coincide and cannot be plotted except as one curve on so small a scale.

Fig. 5 shows a comparison of the two types of curves as obtained from the computations shown on Figs. 3 and 4. From this comparison it is easy to see that the curve having the equation $y = 396{,}445x^{-1.84149}$, or a logarithmic curve, is the best curve to use for estimating the future production of this property, and is undoubtedly the type of equation that would be invariably selected to represent any production decline which shows similar characteristics.

Two Types of Curves Compared

The examples worked out show that if production decline belongs to the percentage-curve type, two engineers estimating the reserves for a given property should arrive at exactly the same result by applying the mathematical method outlined. But, that the results thus obtained will necessarily be nearer the true reserves than those obtained by graphic methods, cannot be definitely affirmed, for innumerable geologic and other factors affect the production of an oil well, of which the engineer has no knowledge, and over which he has no control.

For curves of the logarithmic type, two engineers will arrive at the same result only if they use the same value of x for a starting point. In determining the curve of this type shown in Fig. 4, the equation arrived at represents the best curve for the given data so long as x is given an integral value. However, if fractional values are taken, such as 4.8, 5.8, 6.8, etc., instead of 5, 6, 7, etc., as used, an even closer approximation curve may be found to represent the decline. In fact the writer computed another equation of the same type for this property using the values for x indicated above, and arrived at an equation, $y = 339{,}008x^{-1.78868}$, which actually satisfies the given conditions a little better than the equation computed in Fig. 4.

This brings up the objection to a mathematical consideration of the logarithmic curve that a number of trial computations are necessary to arrive at an equation which satisfies the degree of precision desired; and inasmuch as the labor involved in carrying out the necessary calculations is great, in most instances this method is prohibitive.

The following conclusions may, therefore, be drawn:

Decline curves may be determined by the method of least squares with precision for production that declines at a constant rate or follows a percentage curve; hence this method may be used where time permits and the best possible curve is desired.

For production declines following the logarithmic type of curve, a number of trial computations are necessary to determine the best curve within the limits of precision assigned; hence it is questionable whether

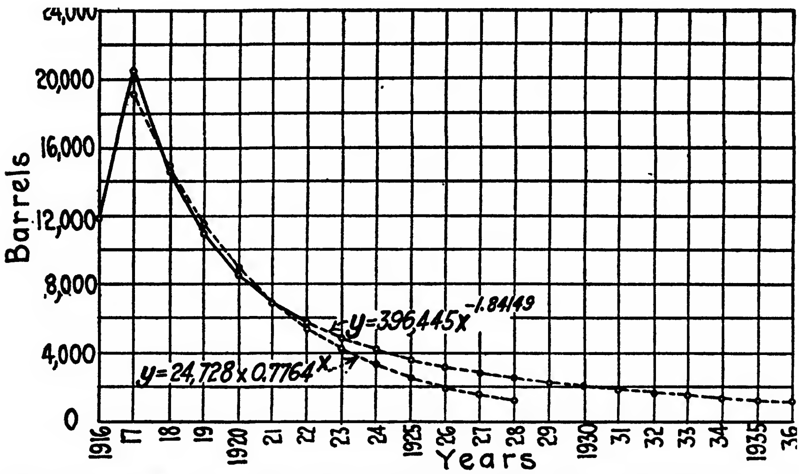

FIG. 5.—PROPERTY IN SEC. 12, T. 21N., R. 12E., TULSA COUNTY, OKLA.

or not it is worth while to use the method of least squares in working out curves of this type, especially in view of the fact that, with care, almost the same result may be arrived at graphically by the use of logarithmic cross-section paper.

Comparative Study of Well Logs on the Mexia Type of Structure

By Frederic H. Lahee,* Ph. D., Dallas, Tex.

(New York Meeting, February, 1925)

The purpose of this paper is to demonstrate the similarity of the oil-producing structures in the Mexia[1] fault zone, and to show how the apparently very irregular well logs in these fields may be used for the practical interpretation of subsurface conditions.

The Mexia oil field, in Limestone County, Tex. (Fig. 1) is closely associated with a fault that trends about 30° east of north and has a displacement of between 200 and 400 ft., with downthrow on the west. Minor slips accompany this major fault, some being roughly parallel to the main break while others are transverse to it. These faults belong to the so-called *Mexia fault zone*, a belt of fracturing that has been traced in its characteristic features southward to near Kosse, 15 miles south of Groesbeck, in southern Limestone County, and northward at least as far as the Trinity River at the eastern border of Navarro County, and possibly as far north as Hunt and Hopkins counties.[2]

The *Balcones fault zone*, from 30 to 40 miles west of the Mexia fault zone, differs from the latter in that its principal displacement is a downthrow on the east. In this respect, it is exactly the opposite of the Mexia displacement. Between these two zones of major faulting lies a great down-dropped block, or graben, which is broken by numerous minor faults.

Oil Fields Associated with Mexia Fault Zone

When speaking of oil fields associated with the Mexia fault zone, we refer only to those now producing from the Woodbine sand. In this category belong the Mexia, Currie, Old Richland or Seay-Cranfill, Powell, and New Richland fields, named in the order of their discovery (see Fig. 1). Subsequent development may prove that the gas found in the Boyd Oil Co.'s Connor well, north of Kerens, is coming from another pool in the same fault zone.

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* Chief Geologist, Sun Oil Co.

[1] Pronounced "Meh-heé-á," the x being sounded as h and the i as ee.

[2] F. Julius Fohs and H. M. Robinson: Structural and Stratigraphic Data of the Northeast Texas Petroleum Area. *Econ. Geol.* (1923) 18, 709.

The Mexia Oil Field[3]

In October, 1920, the Humphreys Oil Co., drilling on the Mexia anticline, as it was known at that time,[4] under the advice of F. Julius Fohs, discovered oil at a depth of approximately 3000 ft. in the Woodbine sand near the base of the Upper Cretaceous system.[5] The first few locations were made with the object of testing this fold. As other wells were drilled, it gradually became evident that the oil in the Woodbine sand here owed its accumulation not so much to a simple anticline as to a major fault with attendant drag. The logs of wells have shown that the western edge of the pool is sharply defined where the Woodbine sand is cut by the Mexia fault (see Figs. 2 and 3). In some parts of the field this fault has a westward dip of 35° or 36° in the formations above the Austin chalk, but increasing to 50° or more from the top of the Austin chalk downward. Toward the northern and southern ends of the field either this fault steepens or it is intersected by other steeply dipping faults. The details of the structure at the two ends of the Mexia pool have not been thoroughly investigated by the writer.

The relationship between accumulation and faulting at Mexia has been clearly established by subsequent development. The largest gushers were not far from the line where the pay sand is cut by the fault. In many instances, the western offset to a big well was found to be a dry hole if it happened to be drilled across this line. Eastward, the average flush production of the wells diminished to the eastern margin of the pool. The oil in the Mexia field is between 35° and 36.5° Bé. at 60° F.

The maximum structural relief of the producing part of the Mexia structure is about 150 ft. Edge water was found between 2540 and 2550 ft. below sea level.

The Currie Oil Field

Structural conditions in the Currie field have been described elsewhere by the writer.[6] In brief, the production, which is contained in certain sands of the Woodbine formation at a depth of about 2950 ft., is banked up against a fault of the Mexia type, with a westward dip of between 45° and 60°, a strike about 20° east of north, and a displacement of 250 ft. or more, with downthrow on the west (Figs. 4 and 5). The discovery

[3] W. E. Pratt and F. H. Lahee: Faulting and Petroleum Accumulation at Mexia, Texas. *Bull.* Amer. Assn. Pet. Geol. (1923) 7, 226.

[4] Mapped by George C. Matson on the shallow gas sand. See U. S. Geol. Surv. *Bull.* 629 (1916).

[5] The formations encountered in this general area, going downward, are: Midway (Eocene), up to 600 ft. or more; Navarro-Taylor shale and marl formation, 2000 to 2200 ft.; Austin chalk, 385 to 475 ft.; Eagle Ford shale, 210 to 425 ft.; and Woodbine formation, including chiefly sandstones and sandy shales, 300 to 400 ft.

[6] The Currie Field, Navarro County, Texas. *Bull.* Amer. Assn. Pet. Geol. (1923) 7, 25.

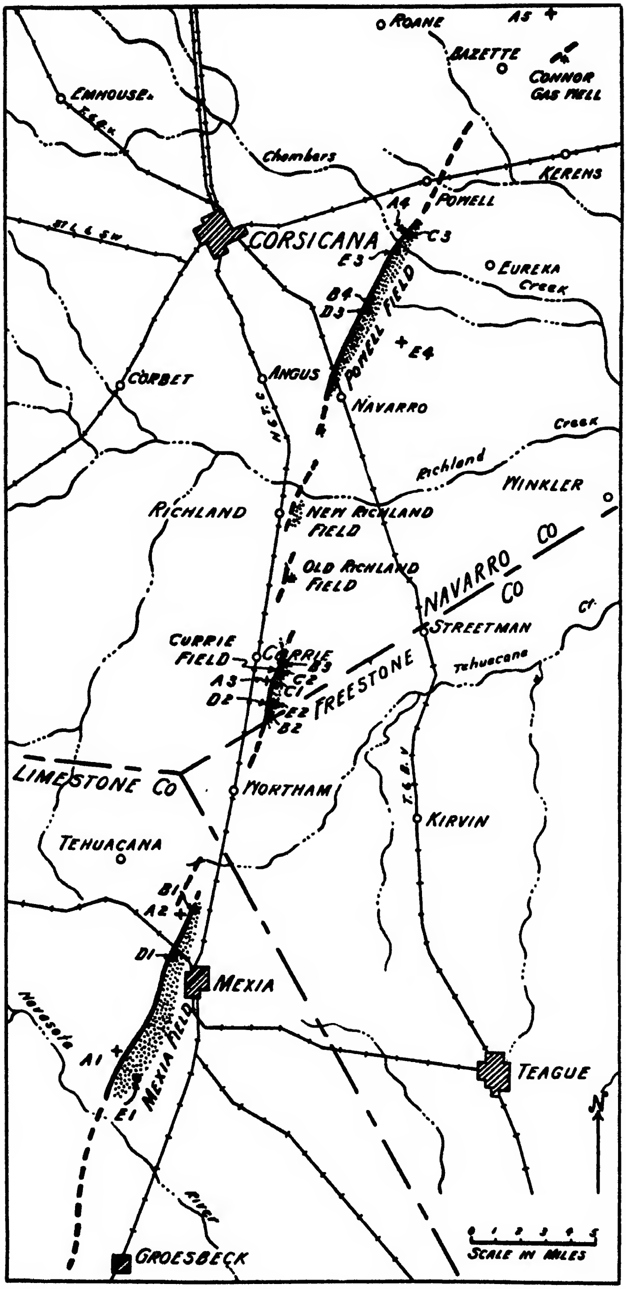


Fig. 1.—Distribution of oil fields in Mexia fault zone; lettered and numbered points indicatea pproximate locations of the wells of which logs are shown in Figs. 9 to 13.

FIG. 2.—SKETCH MAP OF MEXIA OIL FIELD, SHOWING LINE *AB* OF SECTION DRAWN IN FIG. 3; THIS MAP WAS TRACED FROM A MAP FURNISHED BY THE TEXAS PRODUCING DIVISION OF THE PURE OIL CO.

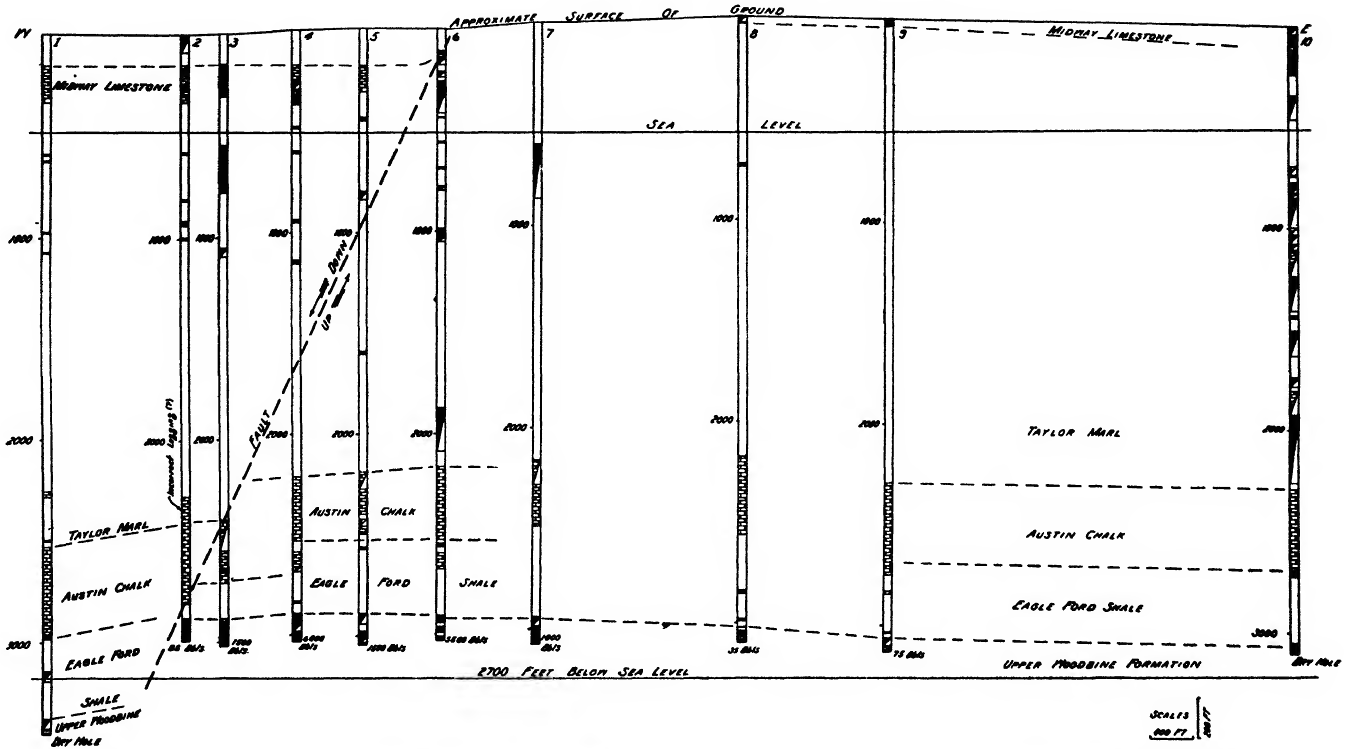


FIG. 3.—VERTICAL SECTION ACROSS MEXIA FIELD; SEE FIG. 2 FOR LOCATION OF WELLS; FOR LEGEND, SEE FIG. 9. AS VERTICAL SCALE IS TWICE THE HORIZONTAL, DIP OF FAULT IS TOO GREAT; IT SHOULD BE ABOUT 49°, BUT THIS ANGLE IS AN AVERAGE. DATA FOR FIELD INDICATE THAT DIP IS LOWER ABOVE THE TOP OF AUSTIN CHALK THAN BELOW THIS HORIZON. IN FIG. 7, NATURAL SCALE IS USED. LOGS ARE RECORDS OF FOLLOWING WELLS: 1, HUMBLE OIL & REFINING CO.'S NUSSBAUM 1; 2, TEXAS CO.'S HARRIS 4; 3, REPUBLIC PRODUCTION CO.'S SLAUGHTER 2; 4, GULF PRODUCTION CO.'S SLAUGHTER 1; 5, HUMPHREYS-MEXIA OIL CO.'S DANCER 5; 6, *ibid.*, DANCER 6; 7, *ibid.*, BERTHELSON 27; 8, *ibid.*, BERTHELSON 16E; 9, *ibid.*, BERTHELSON 3E; 10, E. L. SMITH'S MCGRAW 1.

well, known as Meador 1, was drilled by the Humphreys-Mexia Oil Co., in the fall of 1921, the location having been made by Mr. Fohs and his geological staff. As in the case of Mexia, this well was located on an anticline, but the fold is relatively small and poorly exposed. The proximity and relations of the big fault were not known until drilling revealed

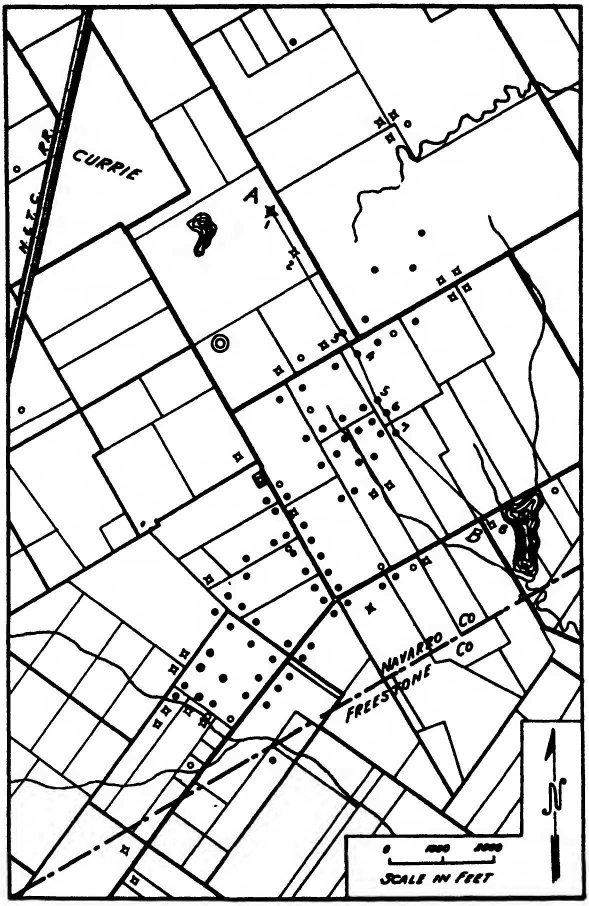


FIG. 4.—SKETCH MAP OF THE CURRIE OIL FIELD, SHOWING LINE *AB* OF SECTION OF FIG. 5; TRACED FROM MAP FURNISHED BY TEXAS PRODUCING DIVISION OF THE PURE OIL CO.

the deep subsurface conditions. The oil is about 41° or 42° Bé. at 60° F. The maximum structural relief of the producing part of the structure is about 50 or 60 ft. Edge water was found at a depth of about 2540 ft. below sea level.

The Seay-Cranfill Gas and Oil Field

The extent of the Seay-Cranfill, or Old Richland, field has not been determined. The discovery well, estimated to have yielded a flush of

over 50,000,000 cu. ft. of gas per day, was completed in January, 1922. It was drilled at a point where, as in the case of the Meador 1 at Currie, there seemed to be indications of a small anticlinal fold. This location was selected by D. J. Edson, of the Humble Oil Co. Subsequent drilling disclosed that this small fold is associated with a fault simi-

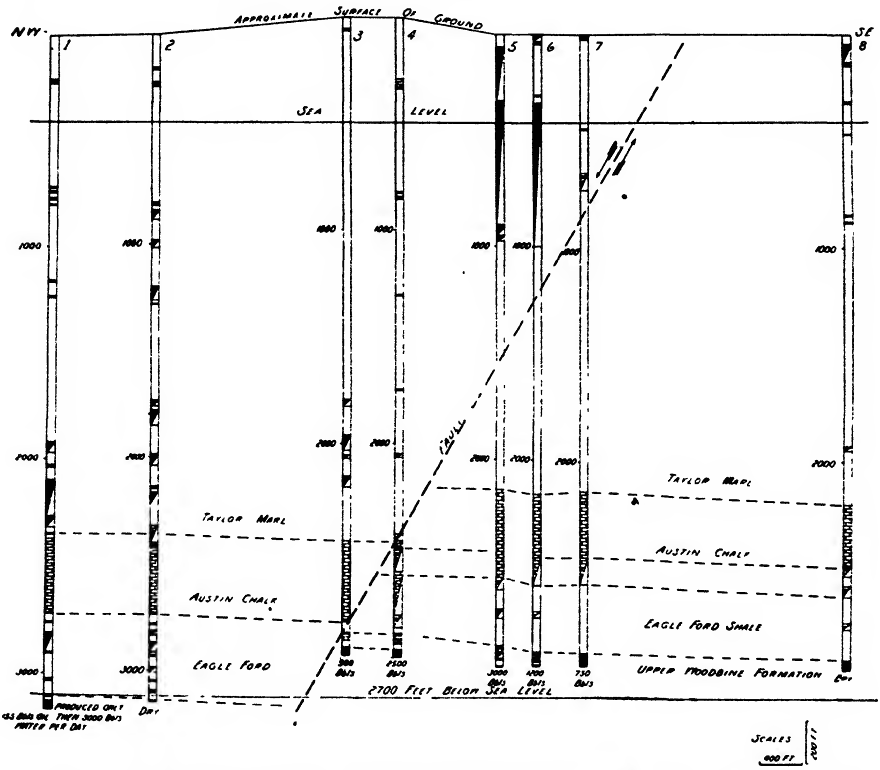


FIG. 5.—VERTICAL SECTION ACROSS CURRIE FIELD. SEE FIG. 4 FOR LOCATION OF WELLS; FOR LEGEND, SEE FIG. 9. TRUE AVERAGE DIP OF FAULT HERE WOULD BE ABOUT 41°, IF VERTICAL SCALE WERE NOT EXAGGERATED. SEE FIGS. 3 AND 7. THE LOGS SHOWN ARE: 1, HUMPHREYS OIL CO.'S GARRETT 1; 2, *ibid.*, GARRETT 2; 3, *ibid.*, ENGLISH 1; 4, *ibid.*, COLE 1; 5, *ibid.*, COLE 4; 6, *ibid.*, COLE 2; 7, *ibid.*, MEANS 1; 8, MCCABE *et al.*, STUBBS 1.

lar to the Currie fault. The displacement here is 250 ft. or more.[7] Production, consisting of both gas and oil (40° to 41° Bé. at 60° F.) as at Currie, comes from the Woodbine sand at depths between 2950 and 3000 ft.

The Powell Oil Field

The Powell field, remarkable for the rapidity with which it was developed and for the huge daily yield when its production was at the

[7] Recently proved to be fully 400 ft. in the Sun Oil Co.'s gas well on the Swink lease, about 2000 ft. south of the original production.

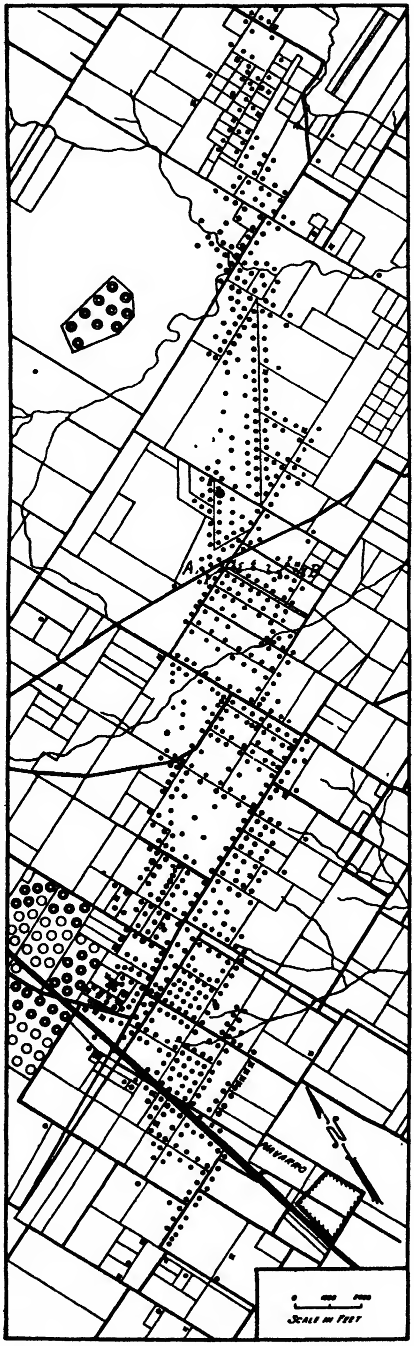


FIG. 6.—SKETCH MAP OF POWELL OIL FIELD, SHOWING LINE *AB* OF SECTION DRAWN IN FIG. 7; TRACED FROM MAP FURNISHED BY TEXAS PRODUCING DIVISION OF THE PURE OIL CO.

peak,[8] is bounded on the west by a fault of the Mexia type with a displacement of at least 400 or 500 ft. (Figs. 6 and 7). Production in the Woodbine formation is obtained from depths between 2800 and 2900 ft. The oil has a gravity of about 36° Bé. The maximum structural relief of the productive part of the structure is about 150 ft., decreasing

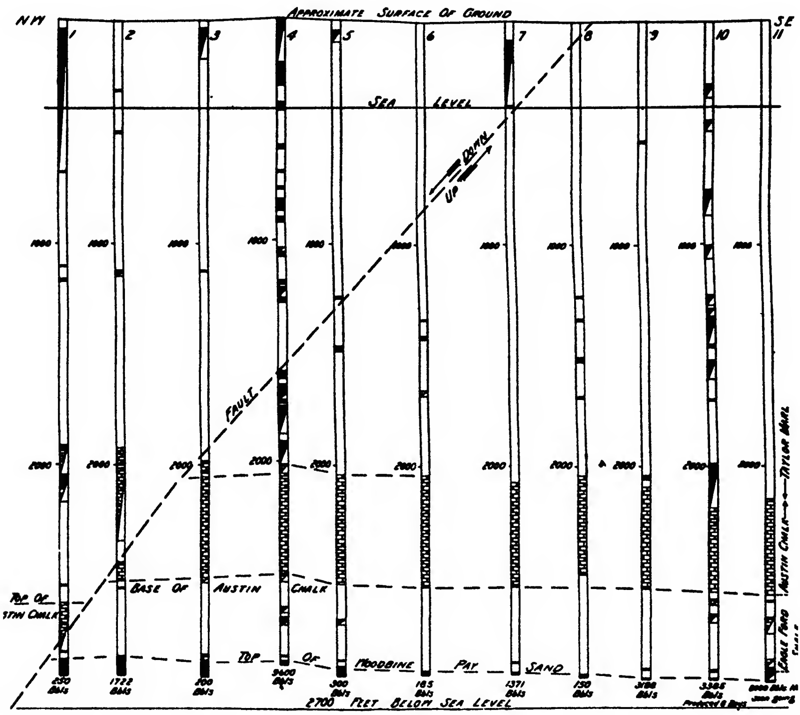


FIG. 7.—VERTICAL SECTION ACROSS THE MIDDLE PART OF THE POWELL OIL FIELD; SEE FIG. 6 FOR LOCATION OF SECTION; FOR LEGEND SEE FIG. 9. LOGS USED ARE: 1, HUMBLE OIL & REFINING CO.'S MCKIE 10B; 2, ROXANA PETROLEUM CORPN.'S MCKIE 5A; 3, ROXANA PETROLEUM CORPN.'S MCKIE 1A; 4, HUMBLE OIL & REFINING CO.'S GENTRY 1B; 5, HUMBLE OIL & REFINING CO.'S GENTRY 3B; 6, HUMBLE OIL & REFINING CO.'S GENTRY 11A; 7, HUMBLE OIL & REFINING CO.'S GENTRY 6A; 8, GULF OIL & REFINING CO.'S GENTRY 4; 9, HUMBLE OIL & REFINING CO.'S GENTRY 4A; 10, HUMBLE OIL & REFINING CO.'S GENTRY 3A; 11, CRANFILL & PENN'S GENTRY 1.

northward from near the southern end of the field. Edge water was found between 2580 and 2600 ft. below sea level.

The discovery well was completed in January, 1923, by the Corsicana Deep Well Co. on the Burke land about 1¼ miles south of the town of Powell. It was located a short distance down the flank of a small,

[8] Over 350,000 bbl. per day in the third week of November, 1923.

pronounced anticline that was mapped by Matson and Hopkins on the shallow oil-bearing sand of the Burke Pool.[9] Again, the association of this fold with a major fault of the Mexia type was not proved until after several holes had been drilled. Because the Burke discovery well was down a little from, and southwest of, the top of the anticline in the shallow oil sand, the concensus of opinion at first was that the field would extend northeast. However, from the logs of a few dry holes drilled to the southwest, several geologists decided that a major fault passed somewhere near the town of Navarro, and checkerboard protection acreage was purchased accordingly. Finding the Woodbine pay sand unexpectedly high in wells drilled southwest of the Burke production soon caused an intensive leasing campaign in this direction and, eventually, the development of the pool southwestward as far as the town of Navarro.

The New Richland Oil Field

The discovery well in the New Richland field was completed in December, 1923, by McDonald Bros. on the A. N. Brown land. By drilling, this latest pool in Navarro County has been shown to be attached to a great fault of the Mexia type with a dip of 55° or 60° toward the west, and with a downthrow on the west amounting to 500 ft. or more. Production in this field is obtained from the Woodbine sand at depths between 2900 and 2960 ft. The oil is about 38.5° Bé. at 60° F. The maximum structural relief of the producing part of the structure is between 30 and 50 ft. Edge water was first found between 2610 and 2615 ft. below sea level.

Importance of Mexia Type of Structure

In reviewing the general characters of these oil fields, one is impressed by the peculiar, yet definite, structural conditions that attend the petroleum reservoirs, and also by the close resemblance of these conditions in all the pools within the Mexia zone. Although, before the Mexia field was developed, the Mexia type of structure—a strike fault with upthrow on the side toward the regional dip of the strata—was regarded by geologists as possibly favorable to oil accumulation, its great economic importance in the Mid-Continent region was not fully appreciated until within the last three years. During these years, much time and money have been spent in seeking similar faults, but, outside of the Mexia fault zone as just described, the only fields recently developed that seem to be associated with the same kind of displacement are the Luling field of

[9] George C. Matson and Oliver B. Hopkins: The Corsicana Oil and Gas Field, Texas. U. S. Geol. Surv. *Bull.* 661 (1917) 211.

Caldwell and Guadalupe Counties,[10] and the chain of pools in the Mirando district of Webb County, Tex.[11]

Dimensions of Pools of Mexia Type

It is characteristic of pools of the Mexia type that they are relatively long and narrow. This is because the oil has accumulated along and close to the fault. The dimensions of the pools to which we have referred are as follows:

Name of Pool	Length along Fault, Miles	Maximum Width
Mexia	7	1¼ miles
Currie	2	2800 feet
Powell	7½	4000 feet
Luling	7½	4000 feet
Mirando group	At least 25	5000 feet

Luling and the Mirando group have been included for comparison. The Old and New Richland fields are omitted because their limits have not been sufficiently determined.

Poor Exposure of Major Faults at Earth's Surface

In spite of the large displacement of the major faults that have controlled the accumulation of oil and gas in the pools of the Mexia fault zone, these faults are seldom clearly exposed at the surface of the ground. At Mexia, the displacement is indicated along part of its extent by the rather abrupt westward termination of outcrops of the Midway limestone along a fairly straight line, by steep westward dips of this limestone along its western edge, and by occasional indications of slickensiding. North of the Mexia field, another fault may be readily located near Tehuacana creek.[12] In a few scattered outcrops, northward in the zone, steep or irregular dips suggest faulting. With these few exceptions, however, the actual position of the surface trace of each of these big faults is very obscure. In the early days of the development, when dips and strikes were sought in actual rock outcrops and field work was carried forward rapidly, evidences of faulting that have since been found were almost if not quite overlooked. We now know that a careful study of the Midway stratigraphic section reveals several members that can be recognized and traced for miles along their strike. In many places

[10] W. E. Pratt: Oil at Luling, Caldwell County, Texas. *Bull.* Amer. Assn. Pet. Geol. (1923) 7, 182. The discovery well of the Luling field, drilled by the United North & South Oil Co., was located on the recommendation of Vernon Woolsey, geologist, who found the controlling fault and mapped the structure.

[11] Production at Luling is from the Georgetown, or upper part of the Edwards limestone, of Lower Cretaceous age, reached at depths near 2150 ft.; production at Mirando is found principally in the Cook Mountain formation of Tertiary Age, at depths of 1500 to 2000 ft.

[12] This fault is associated with the Wortham pool, discovered late in November, 1924, through the work of the geological department of the Boyd Oil Co.

formerly regarded as "soil covered," a repetition of these Midway members can be found, thus indicating, within a hundred feet (though more often, within several hundred feet), the approximate position of the big faults.

An interesting fact brought out in the study of these faults is that their displacement is less in the Tertiary than in the Cretaceous strata. In some cases, where the Austin chalk has been downthrown 400 or 500 ft., the same fault has displaced the overlying Midway apparently not over 100 or 150 ft. Some geologists have attributed this feature to a gradual lessening of the displacement upward through the relatively soft Taylor and Navarro formations above the Austin; but while this may account for some of the decrease, the principal explanation is that there was some movement on these faults before the Midway was deposited and the displacement of the Tertiary beds was due to further slipping on preexisting buried fracture surfaces.[13] There is a possibility, not yet demonstrated as far as we know, that the post-Midway movement in these deep fractures, which cut the Cretaceous and older rocks, was distributed through the Tertiary beds in several faults, focusing, as it were, at the pre-Midway trace of the old faults.

Interpretation of Subsurface Conditions

Practical Importance of Subsurface Study

In oil-producing territory where surface exposures are poor, as in the Mexia fault zone, the study of subsurface conditions by means of well logs becomes of prime importance. It is true that some well logs are so poor that they are useless and that others are difficult to interpret; and for this reason some so-called "practical oil men" are inclined to cast aside all logs as of no value. This perhaps has been especially true of the Mexia fault zone records, which have differed so greatly and apparently without reason. The blame was at first placed on the driller (whom we admit is often too careless in keeping the records of the formations he penetrates), but too much undue criticism has been placed on the logs of wells in these pools. These logs vary, of course, but most of them can be interpreted within a limit of error that is small in comparison with the practical facts determinable in their correlation. In the fields of the Mexia fault zone, the value of intensive study of the well records is great.

Comparison of Logs of Different Fields

As already stated, the main controlling fault in each of the fields in the Mexia fault zone strikes from 20° to 30° east of north, nearly parallel to the regional strike of the beds; they dip usually at angles between 45° and 65° toward the west and have the downthrow on the side up the regional dip of

[13] The Midway rests disconformably upon the Cretaceous in this part of Texas, the surface on which the Midway beds were laid down having been markedly irregular.

the strata; they therefore are accompanied by drag downward toward the west in the eastern or upthrown block. In every instance, the oil has accumulated against the fault in the upthrown block.

These conditions are diagrammatically shown in Fig. 8. The lettered vertical lines represent wells corresponding to the logs shown in Figs. 9 to 13. In these figures, like logs have been selected from the Mexia, Currie and Powell districts, and have been placed together for easy comparison. Logs of the same types could have been chosen from the Richland Field.

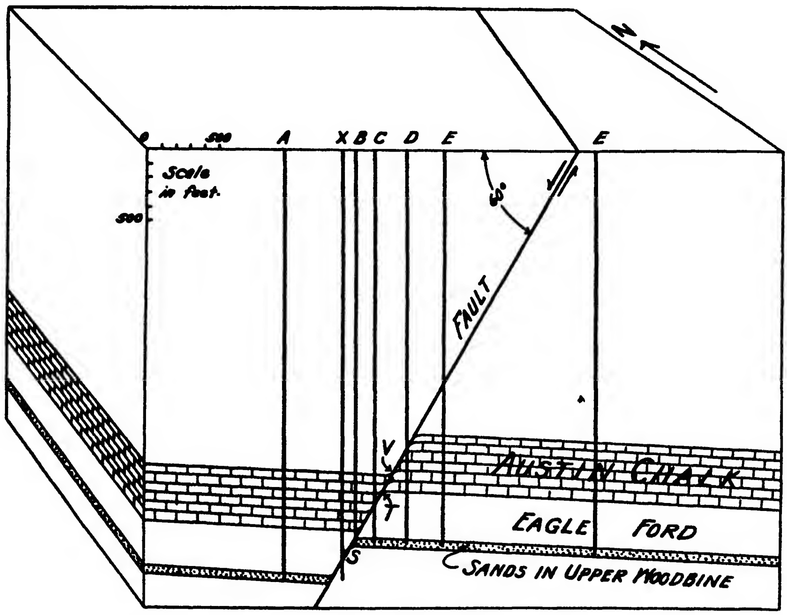


FIG. 8.—DIAGRAM SHOWING GENERAL CONDITIONS ATTENDING FAULT STRUCTURES OF MEXIA TYPE. VERTICAL LINES REPRESENT RELATIVE POSITIONS OF WELLS LIKE THOSE RECORDED IN FIGS. 9 TO 13. LOGS OF FIG. 9 CORRESPOND TO THE WELLS *E* IN FIG. 8, THOSE IN FIG. 10 CORRESPOND TO *D* IN FIG. 8, ETC. TO EMPHASIZE RELATIONS OF THESE WELLS TO STRUCTURE, FAULT IS SHOWN WITH A UNIFORM DIP OF 60° AND THE FAULT TRACE ON THE SURFACE AS A STRAIGHT LINE. FRONT FACE OF BLOCK IS A CROSS-SECTION DRAWN TO NATURAL SCALE.

In Fig. 9 are four logs that display normal relations in the Austin chalk and Eagle Ford shale. The locations of these wells are indicated in Fig. 1. Well *E*4 was drilled far down the regional dip and therefore encountered the formations deeper than in the other three cases. All these wells are situated east of the point where the fault cuts the top of the Austin chalk. Those which are near this point might correspond to the positions marked *E* in Fig. 8.

In Fig. 10, in logs *D*1, *D*2, and *D*3, the Austin chalk has a reduced thickness, but the Eagle Ford has normal thickness; this is because the fault has cut out some of the chalk. Records of this kind would be

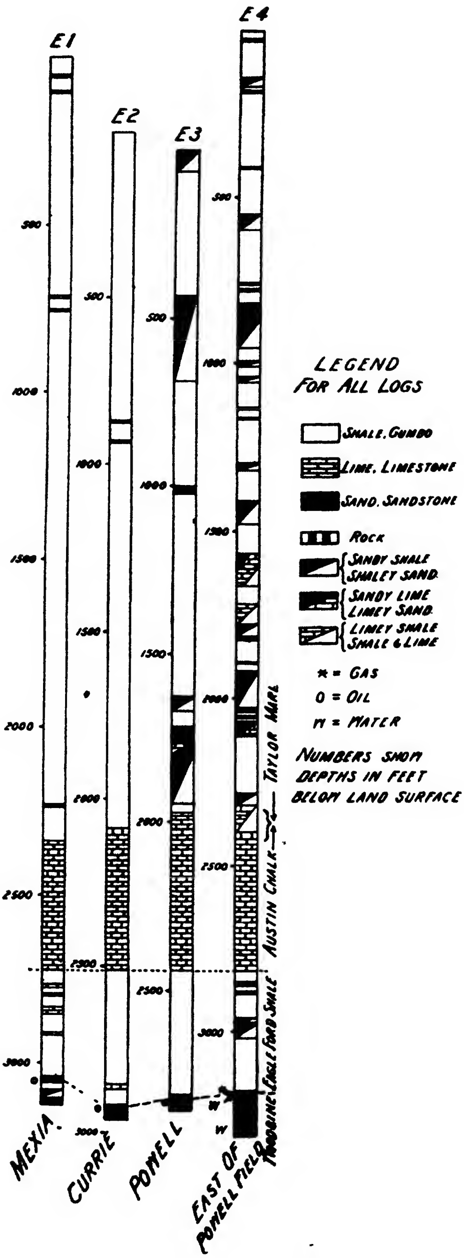


FIG. 9.—LOGS SHOWING APPROXIMATELY NORMAL RELATIONS OF AUSTIN CHALK, EAGLE FORD SHALE, AND UPPER WOODBINE FORMATION. THICKNESS OF THE CHALK VARIES FROM 400 TO 475 FT.; AND THAT OF THE EAGLE FORD FROM 300 TO 400 FT. THE LOGS ARE CORRELATED ON THE BASE OF THE CHALK. THE WELLS ARE: *E1*, WOODBINE OIL CO.'S MANNING 1; *E2*, HUMPHREYS OIL CO.'S M. BOUNDS 3; *E3*, SUN OIL CO.'S KENT 4; AND *E4*, HUMPHREYS OIL CO.'S SINGLETON 1.

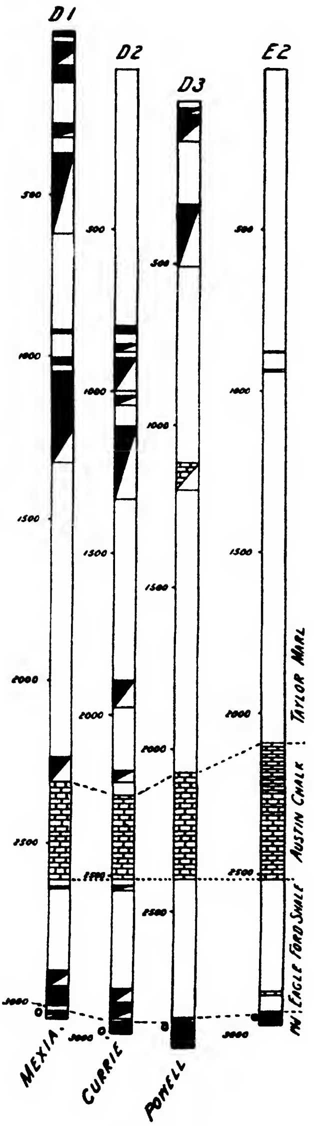


FIG. 10.

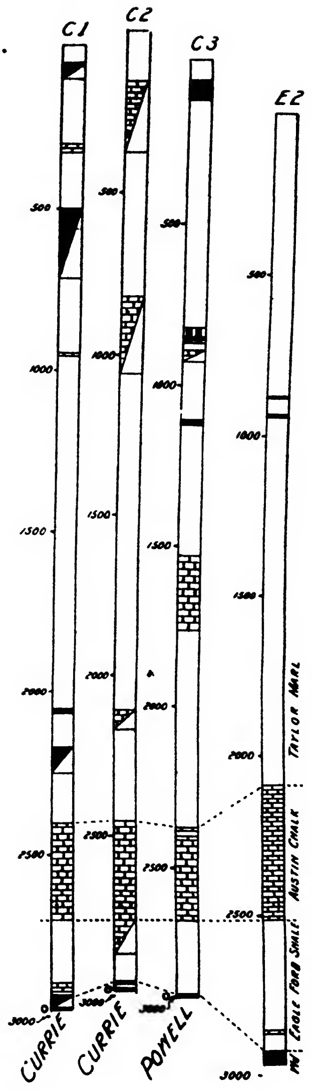
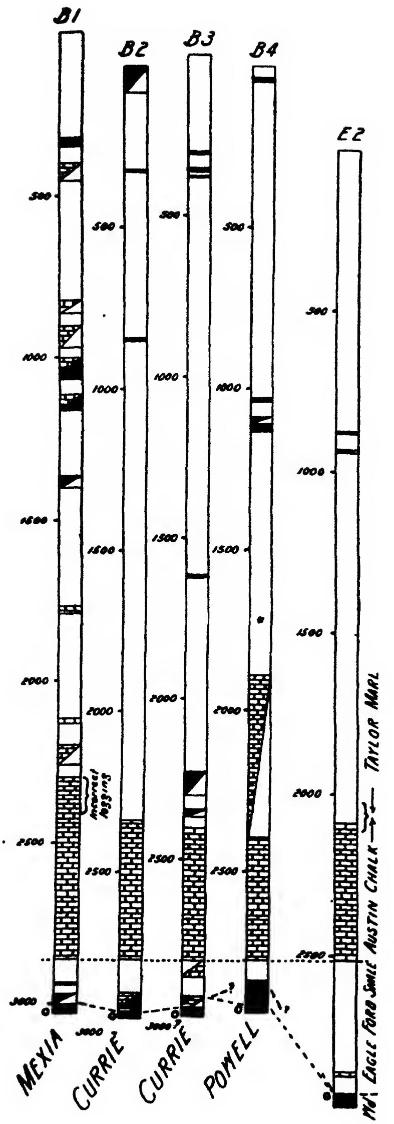


FIG. 11.

FIG. 10.—LOGS SHOWING AUSTIN CHALK WITH REDUCED THICKNESS (HERE 250 TO 325 FT.) BUT EAGLE FORD SHALE OF NORMAL THICKNESS (375 TO 425 FT.). LOG $E2$ IS SHOWN FOR COMPARISON. IT IS THE SAME AS $E2$ IN FIG. 9. THE LOGS ARE OF THE FOLLOWING WELLS: $D1$, ATLANTIC OIL & REFINING CO.'S ROLLER 4; $D2$, GULF PRODUCTION CO.'S R. V. BOUNDS 1; and $D3$, HUMBLE OIL & REFINING CO.'S RAMSEY 13-B.

FIG. 11.—LOGS SHOWING AUSTIN CHALK AND EAGLE FORD SHALE, BOTH WITH REDUCED THICKNESS. THE CHALK IS HERE FROM 280 TO 300 FT. THICK AND THE SHALE IS FROM 180 TO 230 FT. THICK. LOG $E2$ IS INSERTED FOR COMPARISON. THE WELLS ARE: $C1$, HOMA OKLA OIL CO.'S MCGAW 6; $C2$, HUMPHREYS OIL CO.'S MEADOR 5; AND $C3$, HUMPHREYS & KING'S SPRINGFIELD 1.



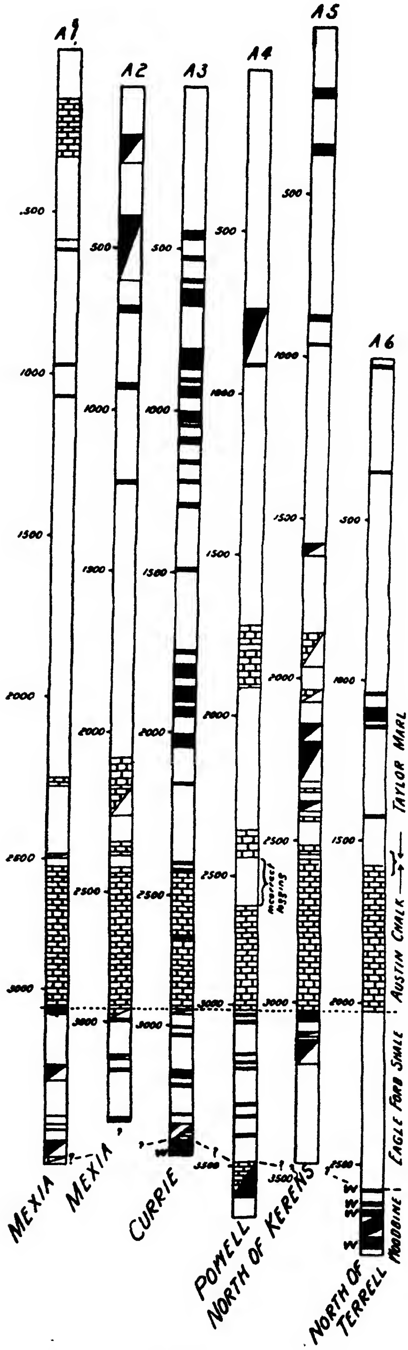


FIG. 12. FIG. 13.

DESCRIPTIONS ARE ON OPPOSITE PAGE.

obtained from the point where the fault intersects the top of the chalk on the upthrown side to the point where it cuts the base of the chalk on the upthrown side. If the throw of the fault (vertical component of the displacement) is as great as or greater than the thickness of the chalk, the top of the chalk in logs of type *D* coincides with the fault surface; but if the throw is less than this amount, the top of the chalk is the fault surface only down to the point where the fault cuts the chalk top in the downthrown block. In log correlations, this fact must be recognized when making estimates of the dip of the fault.

In Fig. 11, logs *C*1, *C*2, and *C*3 show both the Austin chalk and the Eagle Ford shale with less than normal thickness (a normal log *E*2 is inserted for comparison). This condition may be explained by reference to *C*, Fig. 8. Anywhere between the point where the fault intersects the base of the chalk on the upthrown side and the point where it intersects the base of the chalk on the downthrown side, logs of type *C* would be obtained. The base of the chalk here coincides with the fault surface. If the hole were drilled between *T* and *V*, Fig. 8, the fault might pass through some point in the chalk, as logged, yet the log would look essentially like *C*, Fig. 11; if the throw of the fault were greater than the thickness of the chalk, a well might encounter no chalk in the region of *C*, Fig. 8.

In Fig. 12, the *B* logs all have Austin chalk of normal thickness, but the Eagle Ford is thinner than normal (see log *E*2). This condition corresponds to *B* in Fig. 8. The fault must be very near the top of the Woodbine sand in a well of type *B*. If the fault had a throw greater than the thickness of the Eagle Ford, a well at *B* might pass directly from the Austin chalk into the Woodbine, with no intervening Eagle Ford shale.

At *X*, Fig. 8, a well might not encounter the upper part of the Woodbine; it might pass from the Eagle Ford shale into the lower portion of the Woodbine sand or, if the throw of the fault were sufficiently great, it might entirely miss the Woodbine formation.

Fig. 12.—Logs showing Austin chalk of normal thickness (375 to 430 ft.) but Eagle Ford Shale of very much reduced thickness (140 to 150 ft.). Wells with records of this type are usually close to the edge of the pool (see *B*, Fig. 8). For comparison the normal log *E*2 is given. The wells represented are: *B*1, Gulf Production Co.'s Hughes 1; *B*2, Brothers Oil Co.'s R. V. Bounds 1; *B*3, Humphreys Oil Co.'s Meador 6; and *B*4, Humble Oil & Refining Co.'s Ramsey 14-B.

Fig. 13.—Logs of wells drilled west of the fault that limits production. These logs are essentially normal, but the formations are found much lower than in the wells recorded in Fig. 9. The only exception is *A*6, a well drilled several miles west of the Mexia fault zone. The Austin chalk thickness, as here shown, varies from 440 to 475 feet (*A*4 is probably incorrectly logged at the top of the chalk) and the Eagle Ford shale thickness varies from 400 to 540 ft. The latter grows thicker toward the north. The holes here logged are *A*1, Humble Oil & Refining Co.'s Nussbaum 1; *A*2, Humble Oil & Refining Co.'s Adams 1; *A*3, Humphreys Oil Co.'s Price 1; *A*4, J. K. Hughes' Burke 1; *A*5, Wilson Estate's Dodwell 1; and *A*6, Magnolia Production Co.'s Cernoch 1.

In Fig. 13, are logs of several holes drilled in the downthrown block west of the main Mexia fault zone. The first five wells, $A1$ to $A5$, are not far west of the fault, and therefore show the formations low. Well $A6$ was drilled in northern Kaufman County, north of Terrell, several miles up the regional dip of the strata. The log is given merely for comparison. All these logs record the formations of normal thickness; they are very much like those in Fig. 9.

An inspection of the logs in Figs. 9 to 13 shows (1) that in each of the fields records of very similar character are obtained from wells drilled in analogous positions relative to the fault, and (2) that the logs of wells drilled along lines transverse to the direction of the fault may be very dissimilar and still be essentially correct.

Practical Application of Well Records

The following suggestions are made in reference to holes drilled within or near the Mexia fault zone.

1. Suppose that the approximate general trend of the fault zone is known and that a hole is drilled somewhat east of this trend. The log records Austin chalk of normal thickness and distinctly low as compared with the expected depth (see Fig. 9). This hole probably lies a considerable distance east of the fault and possibly east of any oil pool that may be associated with the fault.

2. A hole that is being drilled supposedly in the trend but with the possibility of being west of it does not encounter the Austin chalk until it has reached a surprisingly great depth (see Fig. 13). Often the drillers of wells like this one report high chalk, but as the hole is deepened, this chalk proves to be interrupted by shale breaks and about where the drill should go out of true Austin chalk, it enters the typical chalk and continues in this for 400 ft. more or less, as in the case of well $A4$, Fig. 13. This "high chalk," or Taylor "chalk" is much like the true Austin chalk and has deceived the drillers in many holes that eventually turned out to be dry. Great care should be exercised in guarding against this error. The same mistake was made in the case of many holes drilled far east of the Mexia fault zone, where the Taylor chalk, 800 or 900 ft. above, was thought to be Austin.

3. Suppose that, on a certain property, a well has been obtained producing from the Woodbine sand and that the log shows the Austin chalk and the Eagle Ford shale of normal thickness and at about the depth where they should be in a well several hundred feet east of the fault. On the assumption that the fault has its usual characteristics, the proper procedure in developing the property would be to drill the next location westward (either west, southwest, or northwest, in this region). If this second test revealed normal stratigraphic conditions, the next

well should be drilled again to the west; and this procedure should be followed either to the western boundary of the lease or until the last hole drilled shows relatively thin chalk. With the log as a basis for calculations, whether the next location west of this thin chalk well could be safely drilled may be estimated, assuming that the fault has a maximum dip.

The method is illustrated in Fig. 14. Here *ab* is the Austin chalk in the last well drilled (*N*1), *bc* is the Eagle Ford shale, and *cd* is the producing zone in the Woodbine formation. The record (in the illustration) starts at 1700 ft. below sea level. The figure (except for width of

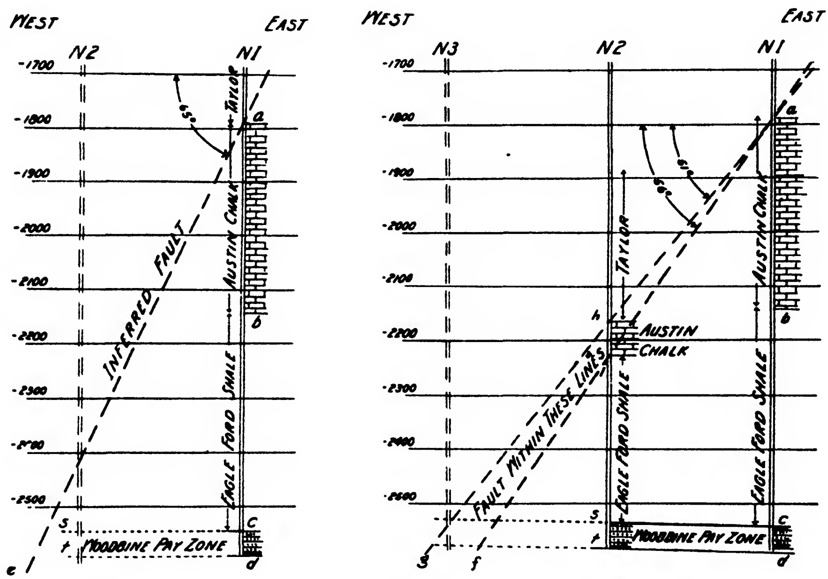


FIG. 14. FIG. 15.

FIG. 14.—GRAPHIC METHOD OF DETERMINING POSITION OF NEXT WELL TO BE DRILLED IN RELATION TO FAULT.

FIG. 15.—SIMILAR TO FIG. 14.

logs) is drawn to true scale, vertical and horizontal. The Austin chalk is only 350 ft. thick, but the Eagle Ford shale has normal thickness. The fault cuts the top of the Austin chalk (see *D*, Fig. 8). Therefore, from *a* draw a line *ae* to represent the fault, making an angle of 65° with the horizontal, which would probably be its maximum dip. At 300 ft. to the west of *N*1 draw *N*2 to represent the position of the next hole that would be drilled, going westward. If the fault line *ae* cuts *N*2 above the probable position of the Woodbine pay zone *st*, the drilling of this well *N*2 is fairly safe.

Suppose that well *N*2 is drilled and that its log shows very thin and rather low chalk. To determine whether another location to the west could be drilled, construct a vertical cross-section (Fig. 15) with the logs

of wells $N1$ and $N2$ plotted correctly to scale. From a (the same as a in Fig. 14), draw ah and ai and produce these lines to g and f, respectively. These lines mark the limits within which the fault must lie, if it is essentially straight in cross-section. We cannot tell whether it cuts the chalk in well $N2$ at h or at i or between h and i. Draw $N3$ to represent a well at the next location westward, here 300 ft. from $N2$. The fault line af

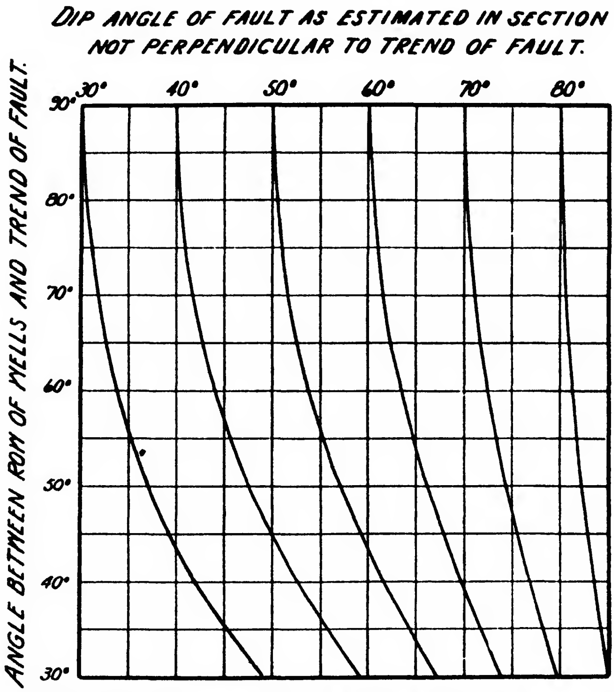


FIG. 16.—CURVES FOR DETERMINING TRUE DIP FROM DIP COMPONENTS MEASURED IN SECTIONS NOT PERPENDICULAR TO STRIKE. SUPPOSE THAT A ROW OF WELLS MAKES AN ANGLE OF 50° WITH APPROXIMATE TREND OF FAULT AND THAT LOGS OF THESE WELLS INDICATE THAT, WITHIN PLANE OF WELLS, THE FAULT DIPS BETWEEN 40° AND 45° WEST. TO FIND APPROXIMATE TRUE DIP OF FAULT: AT TOP OF DIAGRAM FIND 40°, AND FROM THIS POINT FOLLOW DOWN THE CURVE TO ITS INTERSECTION WITH HORIZONTAL LINE MARKED 50°. THIS CURVE CUTS THE 50° LINE ABOUT MIDWAY BETWEEN VERTICAL LINE FOR 45° AND VERTICAL LINE FOR 50°, THUS INDICATING A TRUE DIP OF 47° OR 48°. RESULTS WILL BE ONLY APPROXIMATE SINCE DIPS MEASURED IN SECTION ARE NOT ACCURATE.

would cut the Woodbine pay zone some distance east of location $N3$, and fault line ag would cut this pay zone practically in $N3$. In the first case, $N3$ would probably be a dry hole in this pay zone, and in the second case $N3$ might be dry, or it might be a well in the drag of the pay zone, essentially in the fault. In either case it might run into water under strong pressure, a feature not uncommon in the fault zone. Location $N3$ would therefore best be left undrilled until possibly later development showed that the drag zone was productive in the particular district or that deeper

drilling might penetrate a productive zone below that represented in Figs. 14 and 15 and still east of the fault.

By graphic calculations of this kind, important recommendations have been made either for or against the drilling of offset wells, as the case may be. There is, of course, always a danger of taking the logs too literally. They must be studied with the fact clearly in mind that even those which are most carefully recorded may be incorrect within certain limits of error. Consequently, in correlating, allowance for such errors should always be made on the conservative side. This was the reason for using, in Fig. 14, the maximum probable dip of the fault 65°. The drilling of *N*2, however, demonstrated that the fault dipped not more steeply than 56° and not less than 51° (see Fig. 15).

The dip of the fault is at right angles to the strike of the fault. If the row of wells, such as that considered in the section just described (Figs. 14 and 15) is at right angles to the strike or average trend of the fault, the dip of this fault as shown in the section is virtually correct; but if this row of wells is oblique to the fault trend, the inclination of the fault is less in the diagram, as plotted from well log to well log, than the true dip. Fig. 16 may be used for estimating roughly the true dip of the fault in cases of the latter type.

DISCUSSION

W. A. I. M. van Waterschoot van der Gracht, Ponca City, Okla. (written discussion).—Since this paper was written, a new oilfield has been developed at Wortham, which fills a gap in the string of pools from Mexia to Powell; it is of exactly the same type and entirely corroborates the views expressed in the paper.

Has the author data at his disposal proving that displacement along these faults is less in the Tertiary than in the Cretaceous, as he states on p. 1340? I have always suspected this possibility, but have never been able to obtain proof; the data at my disposal seem to indicate that displacement in the basal Tertiary is not appreciably smaller than in the Austin chalk and, probably, in the Woodbine.

Apparently the long string of Echelon faults, from Mexia to Powell, and probably beyond, is caused by a single large fault in the deeper basement, which, in addition to a vertical displacement, also caused a considerable lateral slip; the eastern part of the block, in all probability, has moved to the north. The movement is probably largely of Laramie age, and is part of a large adjustment that occurred all over the North American continental block during that period.

The correct tracing of the echelon faults in the Cretaceous and Tertiary blanket is difficult, because exposures are few and far between. In consequence it is practically true, as the author states, that only an accu-

rate study of numerous well logs can disclose these structures; and, as more wells are drilled and better logs are kept, our knowledge will gradually become extended. It is not always necessary to drill deep wells but, in many instances, conditions can be revealed by shallow wells drilled to some characteristic key rock, either in the lower Tertiary or the Cretaceous. This is being done by several companies in this territory.

It is now known that south of Mexia the same structural conditions continue all along the rim of the Coastal Plain, against the plateau of Central Texas. Here, however, the Woodbine sand is no longer developed; these sand conditions play out south of the Mexia field, and whatever production is encountered along such faults farther south, as principally is the case at Luling, is obtained from porous streaks in the Edwards limestone. Generally speaking, this is the beginning of the great mass of limestones that develops, ever more prominently, toward the south and is known in Mexico as the Tamasopa; as is well known, it is porous and highly productive in its upper horizons.

North of Powell, more or less similar structural conditions are bound to extend farther to the north; in fact, the logs of a great number of wells prove that such is the case. So far, however, no new oilfields have been discovered in this direction; the well logs, as well as other geological data, rather seem to indicate that conditions to the north are less comparatively simple than in the zone between Mexia and Powell. Apparently, the faults become much more numerous while their individual displacement becomes smaller, although their aggregate amount of throw remains more or less of the same magnitude as the displacement that is concentrated in one single fault zone farther south. In consequence, conditions become very complex farther to the north and it remains yet to be proved whether the smaller amount of displacement, so far established, will suffice to create sufficient accumulation of petroleum in favorable locations along such minor faults. It would seem probable, however, that this should be the case and that other discoveries of oilfields will be made north of Powell, although possibly not of the same importance. A great number of wells have been drilled already in this region though apparently not at the right location. However they prove that, generally speaking, sand conditions remain favorable in the Woodbine horizon.

Accurate study of well logs, along the lines indicated in the paper, will be the only means of finally locating the right spots where production might occur, possibly combined with observations obtained from shallow wells. The author has shown how this territory will have to be worked and has proved that the general idea of the laymen—that the chalk must be encountered high in order to have any chance for production below—is by no means a certain indication for every locality.

Exploration for Petroleum in the Limagne, France

By A. Werenfels, Basle, Switzerland

(New York Meeting, February, 1925)

No petroleum, in commercial quantities, is found in France except the small production of the Pechelbronn field (Fig. 1) in Alsace, which produced 75,000 tons in 1923; therefore the test of the petroleum

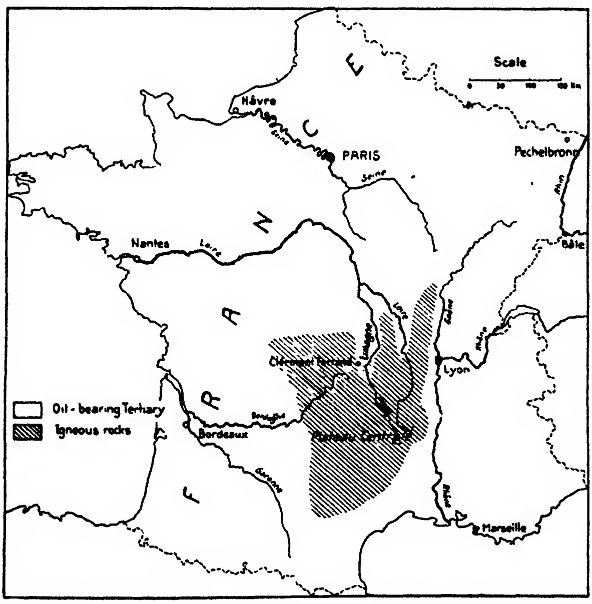


Fig. 1.—Key map.

prospects of the Limagne is most interesting. Under the superintendence of M. Termier, chief engineer of the French mines, a well near Crouelle (Fig. 2) was drilled in 1921 to a depth of 856.3 m. (2808 ft.); at different depths favorable showings were encountered. The well, however, was abandoned because of drilling difficulties. A second one is now being drilled near the same place.

The present paper is the result of the writer's visit to the region in June, 1924, in a party from the Geological Institute of the University of Basle under the direction of Prof. Max Reinhard. The writer regrets being unable to enter as fully into a geological and technical discussion as might be desirable, because of his inability to consult the required references and the scarcity of bibliographic notes.

The Limagne consists of the upper part of the valley of the Allier in the department Puy de Dôme (Auvergne). This valley forms a flat lowland, a graben with an even floor about 45 km. (27.9 mi.) wide, between the two upthrown blocks of the "Chaine des Puy" to the west and the "Monts du Forez" to the east. These two walls belong to the crystalline complex of the Central Plateau of France (Fig. 1), while the graben is formed by Tertiary beds. The two main fault lines bounding the Limagne, as well as the minor faults paralleling them in the interior of the valley, are marked by numerous volcanoes built up at different periods from Oligocene to Pleistocene. Some of these volcanoes consist of cinder cones sufficiently recent to have a crater at their summit; others have been destroyed by denudation and reduced to necks. The majority rise only a few meters above the surrounding flat ground of the valley; the highest (Puy de Crouelle), however, reaches fully 80 m. (262 ft.). The extruded igneous rocks consist of basalt, which is often connected with a neck breccia called "pépérite," which consists of a matrix of basalt and metamorphosed fragments of the same rock and of granite, quartz, marl, and bituminous limestone. Often this breccia is quite well stratified and, in some places, there is evidence of interstratification of the pépérite with layers of metamorphosed Oligocene, which is perhaps caused by intrusion into unconsolidated rocks. However, in general, it seems that the process of intrusion was accompanied by the brecciation of the consolidated country rock, and that this brecciation was followed by a second invasion of the shattered zone by basalt. In many places this breccia is yielding bitumen from fissures and fractures.

Stratigraphy

The formations that outcrop in the Limagne fall under three divisions: volcanic rocks, Tertiary, and Quaternary sediments (see Fig. 2). No special attention is paid to the igneous rocks here. They are treated only as far as their occurrence enlightens the structural features of the region.

The main part of the Tertiary beds of the Limagne belongs to the Oligocene, of which the log of the Crouelle well (Fig. 3) gives a typical stratigraphic section; only the deepest sediments of the Sanoisien (Lower Oligocene) are missing in this section. Near the margin of the basin the Sanoisien consists of sandy clay and arkose; whether the same sediments persist to the interior of the valley is not probable. The lowest deposits

known there consist of shale, clay, and interbedded bituminous limestone (Fig. 3). Only one layer of sand about 0.40 m. (16 in.) thick was found at Crouelle, while at other places thin layers of sandstone beds barren of bitumen are exposed within the same zone of Lower Oligocene. The total thickness of this lagoon deposit is unknown, but is estimated at several hundred meters in the center of the basin.

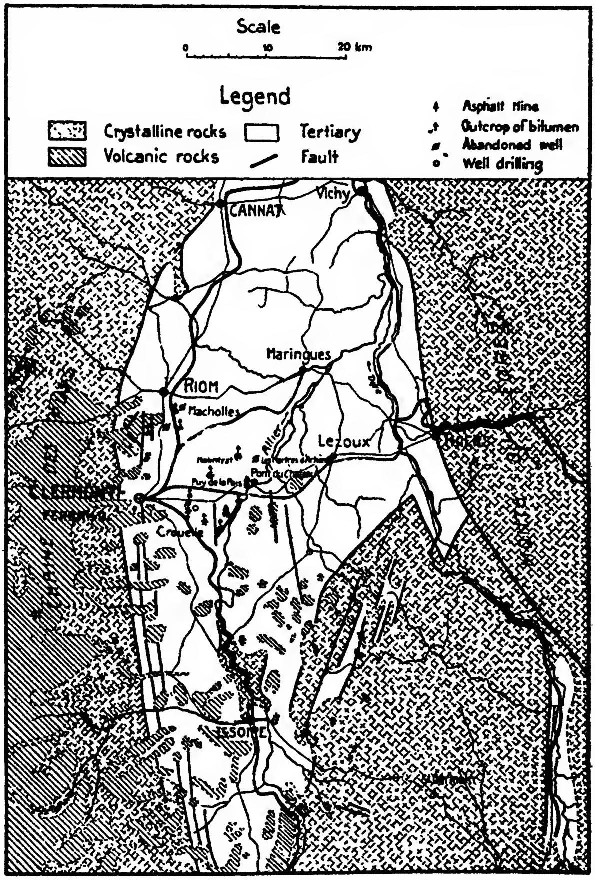


FIG. 2.—GEOLOGICAL MAP OF THE LIMAGNE, AFTER PH. GLANGEAUD.

The Stampian (Middle Oligocene) consists of green, gray, and dark colored marls and limestone, with some shale, clay and little sandstone in it. In the whole series, fossils of brackish and fresh-water organisms are abundant. In the lower zone, anhydrite and some gypsum are interbedded. No real oil-bearing bed is found but bituminous limestone yielding some oil is encountered at different depths.

These near-shore and lagoon deposits of Middle Oligocene age are overlain, in some places, by very similar sediments of the Upper Oligo-

cene (Aquitanien), but no bituminous layers are interstratified in this series.

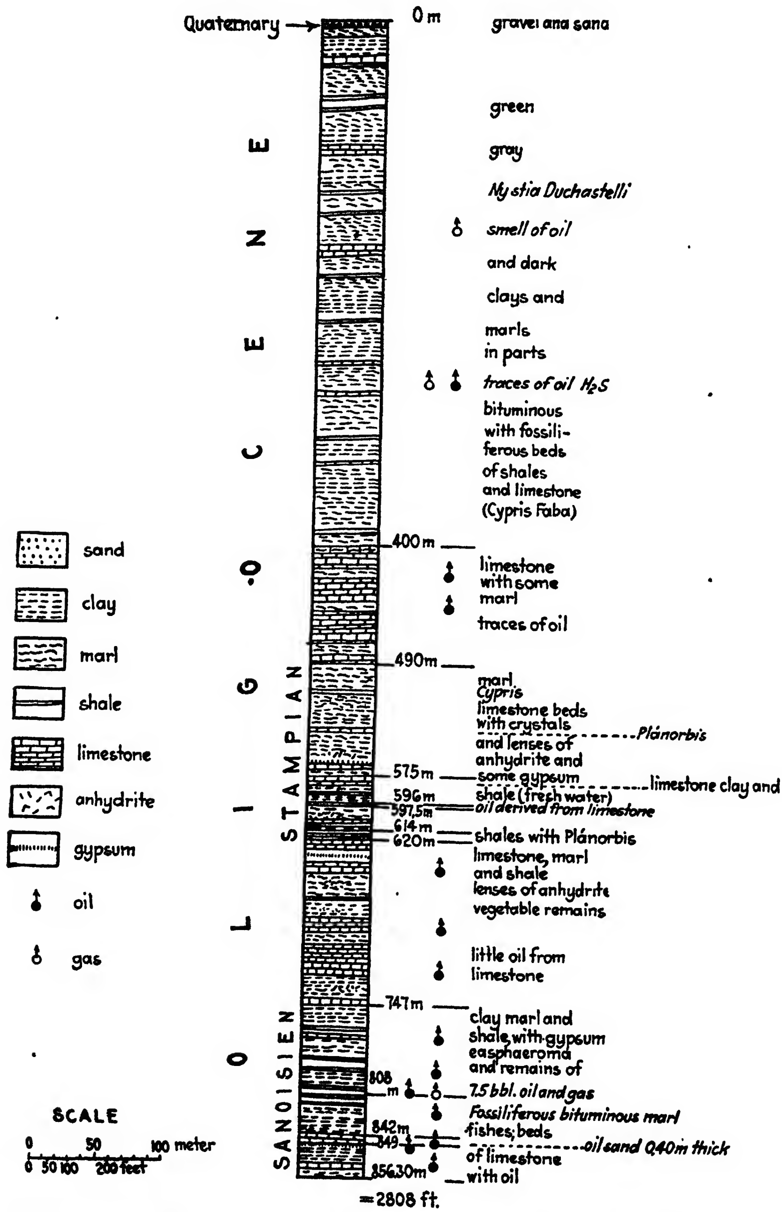


FIG. 3.—OIL WELL "CROUELLE" NEAR CLERMONT-FERRAND, AFTER PH. GLANGEAUD.

The Oligocene sediments are over 1500 m. (4900 ft.) thick; their stratigraphic sequence indicates a general gradual regression of the sea until

the end of Oligocene age, when the Limagne emerged finally and the marine sedimentation stopped. After the Miocene and Pliocene, only fluviatile deposits of sands and gravels are known, and in many places these are overlain by basalt flows or volcanic ash.

Structure

As described, the trough fault of the Limagne forms the major structural feature of the region. The two main bounding fault cliffs are accompanied by many parallel fractures in the interior of the basin, where the fault blocks are already worn down to a peneplain. These minor structural features could provide favorable conditions for possible oil accumulation and retention, but it seems that all these blocks are quite unlevel, even a gentle dipping of the beds within reach of the bituminous layers evidently does not exist and therefore the hope of reaching a reservoir sealed by a fault plane is very small. Other minor uplifts, such as folds, do not occur; however, the existence of a slight updoming of the Oligocene beds around these basalt necks mentioned is not impossible, but even if this intrusion did not cause any doming of the sediments, there will be a disturbed and shattered zone of rocks around these volcanic necks, where petroleum could accumulate in the fissures and openings of the basalt breccia and sediments. These basalt intrusions are, therefore, the only places that deserve consideration with regard to oil accumulation in commercial quantities.

Petroleum

The surface indications of petroleum in the Limagne are limited to an area to the east of Clermont-Ferrand about 10 km. to the north and south of its latitude (Fig. 2). All the seeps are connected with the volcanic necks, where the bitumen is derived from basalt or the volcanic breccia called pépérite mentioned above. A typical seepage is exposed near Malintrat (Fig. 2); where two of these necks occur, each of which rises about 5 to 6 m. (16 to 19 ft.) above the level ground of the Limagne and their diameters vary between 50 and 60 m. (164 and 197 ft.). A black semiliquid bitumen issues from fissures of the pépérite. By inspissation small deposits of asphalt are formed, which were locally exploited. Some of the fractures in the volcanic breccia are sealed by an asphalt breccia, where in a matrix of solid bituminous matter angular fragments of volcanic and sedimentary rocks occur. In some places, pebbles of opal are found in this bituminous dike. Another famous seep exudes at the "Puy de la Pois" (Fig. 2), which is a small neck made up of pépérite and a basalt cone in the center. The seepage of a heavy dark oil issues from fractured pépérite and is associated with a spring of acid water.

For a long time, considerable quantities of asphalt have been mined near Pont du Chateau (Fig. 3), where are layers of well stratified pépérite.

The asphalt is formed by drying out a heavy black oil, which ascends in large open fissures in the pépéritic rock.

All the surface indications of petroleum in the Limagne are, as already stated, connected with volcanic rocks. This fact led some French geologists[1] to the conclusion that the oil originates at deep sources in connection with volcanic processes. In spite of this, there is little doubt that the petroleum comes from the oil-bearing limestone of Oligocene age, from which the pépérite of all of these necks includes large fragments. These petroliferous beds (Fig. 3) are closely associated with anhydrite and gypsum, strata that are assumed to have been formed under conditions that are generally not favorable to the accumulation of organic remains. The series is part marine and part non-marine, the condition when it was laid down changed from marine to non-marine, terrestrial and arid. Similar conditions seem to have existed in the Pechelbronn field (Fig. 1) in Alsace; however, the marine part, adequate to supply material for the formation of petroleum is probably smaller in the Limagne. This predominance of brackish and fresh-water deposits, in addition to the scarcity of proper reservoir rocks, reduces the commercial value of this oil deposit.

The recent exploration for petroleum in the Limagne includes the following wells:

Three abandoned wells: two near Macholles (Fig. 2) the results of which are unknown to the writer and one near Martres d'Artières, where artesian water with carbonic acid was struck.

A shallow hand-drilled well at "Puy de la Pois," which reached a depth of about 20 m. (65 ft.), yielded some barrels of a heavy sticky dark colored oil. The well is located within the zone of the neck breccia, near the center of the cone. It has been abandoned.

The Crouelle well was located between the two volcanic necks of Puy de la Pois and Crouelle, at the border of the highway leading from Bordeaux to Lyon. It was started in the level Tertiary beds of Oligocene age. They were not passed through at a depth of 856.3 m. (2808 ft.), when the casing collapsed, probably owing to gas pressure. As Fig. 3 shows, the drill hole passed through clay, marl, and shale beds with interstratified limestone. The extreme scarcity of sandstone or sands is noteworthy. Only one layer of sand, about 0.40 m. (16 in.) thick, was encountered at a depth of 849 m. (2785 ft.); this sand is 22 per cent. saturated with oil.

Above this sand, some oil issued at different depths from the limestone beds. The gravity of this oil is about 16° Baumé, it contains 9.3 per cent. of sulfur, and the percentage of volatile products at 270° C. is only 16.5 per cent.

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[1] Ph. Glangeaud: "Les Volcans d'Auvergne Clermont-Ferrand," 56. 1910.

The physical and chemical properties of the petroleum from the deeper sand mentioned could not be determined. This Crouelle well was abandoned but a second one is being drilled close to the first location. This well is said to have reached a depth of 1200 m. (3936 ft.). In June, 1924, work was temporarily stopped because of drilling difficulties.

None of these wells is properly located, as they are evidently not within the zone of shattered rocks near the eruptive bodies of one of these volcanic necks. This zone is probably the only place where we may expect oil in commercial quantities; therefore the oil possibilities of the Limagne cannot be considered as having been adequately tested.

Oil Geology of Northern Venezuela

By A. Hamilton Garner,* New York, N. Y.

(New York Meeting, February, 1925)

The occurrence of oil seepages in Venezuela has been known since the early days of Spanish occupation. It was not until 1912, however, that any serious exploration work was undertaken. In that year, the Caribbean Petroleum Co., then a subsidiary of the General Asphalt Co., employed a large staff of geologists to make a systematic survey of large areas in eastern and western Venezuela, selecting the most desirable localities out of the immense area covered by the Valladares concession. This preliminary work was completed in the fall of 1913, and in February, 1914, the company completed its first commercial well at Mene Grande.

Development work has progressed slowly, for various reasons, but petroleum in quantity has been encountered in nine widely separated localities. The Mene Grande field has been put on a producing basis and approximately 4,000,000 bbl. of oil is being shipped annually. Increasing quantities of oil are now being drawn from El Mene and La Rosa. In the light of these developments, the world's need for oil reserves, and the proximity of Venezuela to the United States, American capital is being attracted more and more to Venezuela.

Although considerable careful geological work has been done in Venezuela by the various oil companies now operating, most of the data is buried in the company files, and the published literature has been extremely meager. The most valuable contribution to date has been a map and report by Jahn, which, as it was printed in Spanish, is not generally available to the American oil public.

Venezuela, located in the northwestern part of South America on the Caribbean Sea, lies between 1° and 12° north latitude. Its principal

* Brokaw, Dixon, Garner & McKee, Consulting Geologists.

ports, being only about 1850 miles from New York, are closer to the great Atlantic seaboard refineries than either Tampico or Galveston.

Although it was one of the first countries of the new world visited by the early explorers, the development of its natural resources and its normal increase in population was long retarded by civil wars and a succession of rulers who practiced the theory of "government for the benefit of the governing class." Since the wars of independence which culminated in 1827, and especially since 1910, under the leadership of Juan Vicente Gomez, the country has enjoyed peace and progress theretofore unknown. At present, about 3,000,000 people live within the 400,000 sq. mi. included within its borders. Foreign capital is being encouraged to invest, roads and schools are being built, and nowhere in Spanish America are life and property safer than in Venezuela.

Climate and Topography

The climate, while everywhere characteristically tropical, varies with the topography and is nowhere excessively hot nor abnormally unhealthful. During December, January, February, and March, there is practically no rainfall; the greatest precipitation is in October and November.

In western Venezuela, the region along the northern coast is semi-arid with sparse vegetation. Southward, the humidity increases progressively and from the tenth degree parallel to the southern end of the Maracaibo basin the rainfall is abundant and the country is, for the most part, covered with dense jungles.

In eastern Venezuela, the maximum humidity is less than in the southern part of the Maracaibo basin. The arid strip along the coast, including the mountainous peninsula of Araya, is very narrow. The higher mountains to the south are covered with dense forests.

In the plains of the Orinoco basin, the humidity is greatest in the eastern part. The Orinoco delta is covered with heavy swamp growth. Westward, this gives place to open savannas with a progressive increase in scrub growth, which completely covers the country in western Anzoategui and Guarico.

Northern Venezuela may be divided roughly into three distinct topographic provinces, as follows:

1. The Llanos or Plains Province.—A great plains area of approximately 85,000 sq. mi. covered with grass and low trees. It extends from the Orinoco River north and northwest to the mountains.

2. The Andes.—The eastern Andean Cordillera divides in the southwestern part of Venezuela, one branch extending north along the Colombian border, the other extending northeast across the republic to Caracas thence east along the Caribbean coast. South of Lake Maracaibo, some of the peaks of this range are more than 15,000 ft. high.

3. The Maracaibo Basin and the State of Falcon.—This is the area between the major branches of the eastern Cordillera.

Geology

The methods employed in the study of geology vary in different parts of the country. The best rock exposures are in the beds of streams

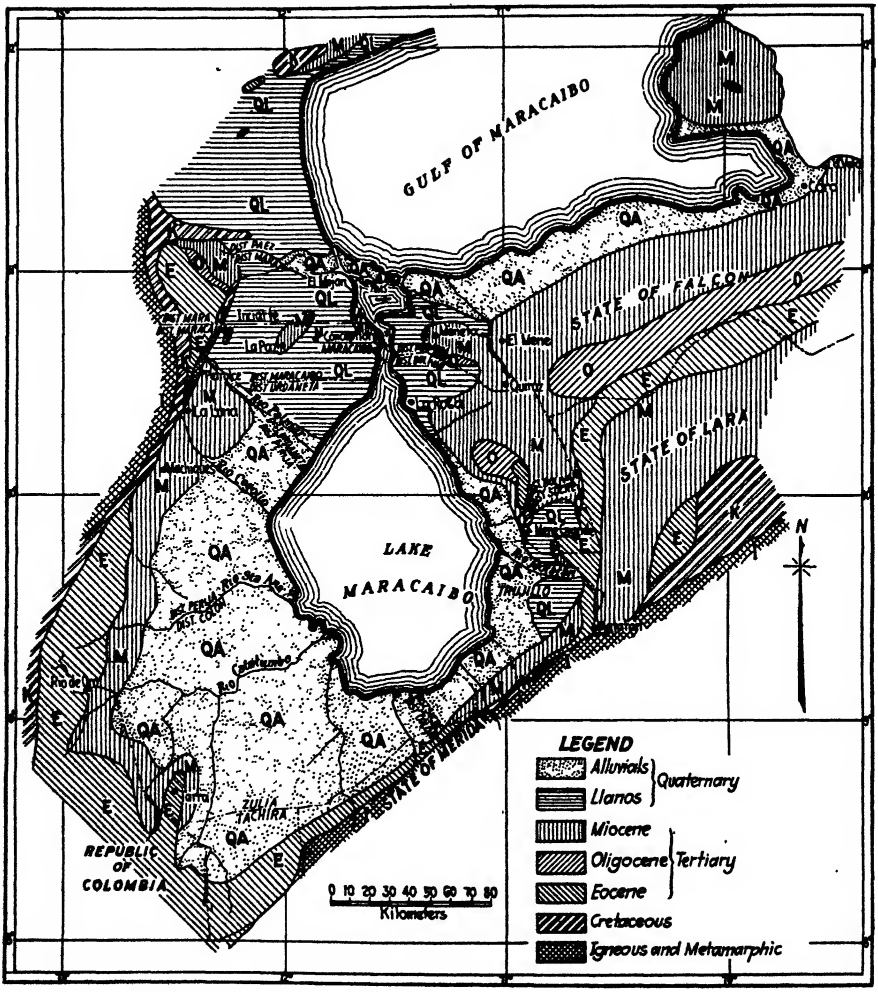


FIG. 1.—GEOLOGICAL SKETCH MAP OF MARACAIBO BASIN.

cutting through the mountains and foothills. Good rock exposures are found also in small hills throughout the central and western parts of the State of Falcon, Fig. 1. Over much of the Maracaibo basin, where there are few outcrops of the more important formations, a system of pit digging has yielded much information on both the character and attitude

of the rocks. Little work of this nature has been done in eastern Venezuela, for most of the geological work has been done near the mountains where there are many exposures.

In both eastern Venezuela and the Maracaibo basin, there is a good opportunity for the use of small core drills. One company has recently started this type of work. It is doubtful if a good marking bed can be found in the Upper Tertiary formations but much valuable information can undoubtedly be obtained.

The rocks exposed in northern Venezuela may be divided as follows: Igneous, metamorphic, Jurassic(?), Cretaceous, Tertiary, and Quaternary.

Igneous Rocks

The principal igneous rocks exposed are pre-Cretaceous, possibly pre-Cambrian granites, porphyries, and basalts. They are found over only a small area in northern Venezuela. No post-Jurassic igneous intrusions have been observed; the exposures of igneous rocks are due to faulting.

Igneous rocks make up the core of the Andes Mountains, with exposures more common to the southwest and less common to the northeast. In the Perija Mountains, on the western edge of the Maracaibo basin, igneous rocks are exposed near Petroleo, District of Perija. Igneous rocks are also exposed near Inciarte and Cachiri, District of Mara; in the northern part of the District of Paez; and on the Island of Toas. No igneous rocks are exposed in the States of Monagas, Anzoategui, or Sucre in eastern Venezuela.

Metamorphics

Metamorphic rocks are exposed over a much larger area than are igneous rocks. They consist largely of mica schists and gneisses of pre-Cretaceous, possibly pre-Cambrian, age. Mica schists make up the major portion of the eastern Andes mountain range and the Peninsula of Araya in eastern Venezuela. Gneisses are exposed along the southern bank of the Orinoco River and make up much of the area to the south in the State of Bolivar. Both schists and gneisses are locally mineralized and bear copper, gold, and lead.

Jurassic(?)

The age of the rocks that are tentatively classified as Jurassic has not been definitely established, but they are placed in this system because they underlie sediments of known Cretaceous age.

The series is made up of fine-grained, well-consolidated, well-bedded sandstones, shales, grits, and conglomerates. The rocks have a distinct red color and are exposed over only a small area in the mountains in the western part of the District of Perija, State of Zulia.

Cretaceous

The rocks of the Cretaceous system are not exposed over a large area in northern Venezuela. They are, however, of great economic importance as certain Cretaceous formations provide a source for much of the oil of the country.

As the lithological character of the formations is persistent, except for minor variations, the Cretaceous rocks are easily recognized. The generalized section for western Venezuela is:

600–1000 ft.	Black, dense, bituminous, hard limestone interbedded with black limy shale; lower shale contains large round limestone concretions; the whole is very fossiliferous and is impregnated with oil. Top of section.
3000 ft.	Very hard, light to dark gray, crystalline, fossiliferous limestone with occasional sandstone beds.
500 ± ft.	Hard, coarse, even-grained, quartzitic sandstone. Base of section.

Various parts of this section are exposed in western Venezuela. A narrow belt outcrops along the northern edge of the Andes Mountains in the States of Tachira, Merida, Trujillo and Lara. In the State of Zulia, it is exposed on the Island of Toas and in the western part of the Districts of Colon, Perija, Mara, and Paez.

Locally, the shales have been altered to slates and the sandstones hardened. This alteration is most pronounced near the Andes and least in western Perija. A generalized section for eastern Venezuela is:

3000 ± ft.	Gray to black, limy shale, with black limestone and sandstone beds in lower part; limestone concretions; fossiliferous; locally impregnated with oil. Top of section.
2500 ± ft.	Hard, light to dark gray, crystalline limestone; fossiliferous.
1000 ± ft.	Hard, quartzitic, coarse sandstone.
500 ± ft.	Black, limy shales. Base.

These rocks, which form a large mountain range in northeastern Anzoategui, northern Monagas and southern Sucre, have been locally altered and hardened. This alteration is most pronounced in the northern part of the area and decreases from north to south. At the southern limit of the Cretaceous area north of Maturin, there is no alteration. In general, the Cretaceous formations withstand erosion and form mountains.

Much oil in Venezuela probably has its origin in the upper formations of this system. Production may be obtained from the Cretaceous only in those limited areas where the upper part of the system carries porous sands.

Tertiary

Exposures of rocks of the Tertiary system are widely distributed throughout the northern part of Venezuela. In the Maracaibo basin, they are found all along the flanks of the mountains and in many localities toward the center of the basin. Exposures are common over the entire State of Falcon.

In eastern Venezuela, they are exposed on the southern flank of the Cretaceous mountains and through the northern parts of the States of Anzoategui and Guarico.

Tertiary rocks undoubtedly underlie the Quaternary in the Maracaibo basin and in eastern Venezuela.

Shales predominate in the Tertiary system with numerous interbedded sandstones and limestones and some coal beds. As most of the sedimentation occurred in shallow water under rapidly changing conditions, the formations vary widely in character and thickness from place to place.

The stratigraphic relation between the Tertiary and Cretaceous has not been definitely established but it is probable that they are separated

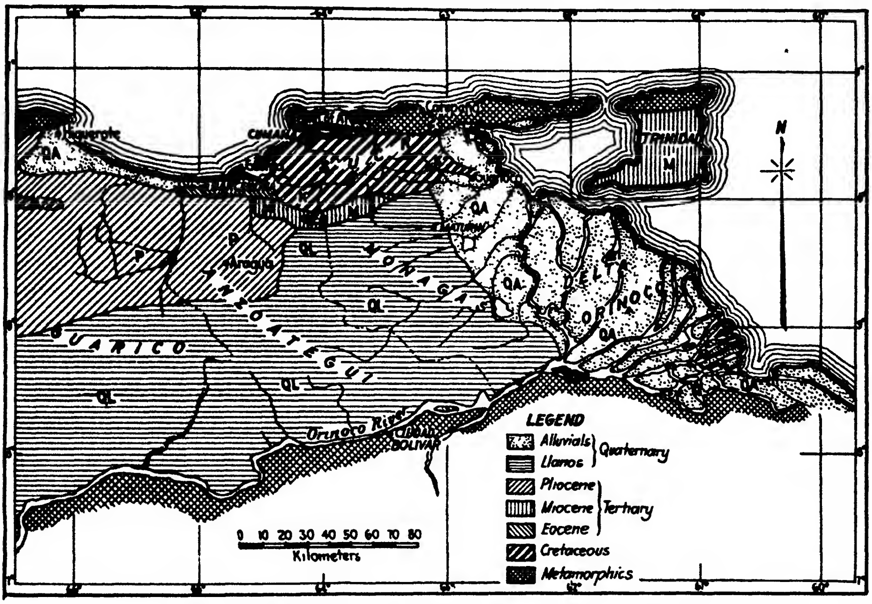


FIG. 2.—GEOLOGICAL MAP OF EASTERN VENEZUELA.

by a small angular unconformity. Faulting is so common near the exposed contact of the two systems that it is usually impossible to find an undisturbed sequence of beds.

Eocene.—The rocks of the Eocene show less lateral variation than the later Tertiary sediments and certain formations with persistent characteristics are widely distributed. A typical section follows:

2000–3000 ft.	Hard, coarse, well-consolidated, massive sandstone, usually light colored with a small amount of dark gray shale; sandstone quartzitic in some localities. Top of section.
1000–2000 ft.	Carbonaceous, brown to black shales, sandy shales and thin-bedded sandstones; in some localities contains thick coal beds.
500 ± ft.	Dark colored shales, fossiliferous limestones and thin-bedded quartzitic sandstones. Base of section.

The Eocene is well exposed in many places along the flanks of the mountains surrounding the Maracaibo basin and is best developed in western Colon, southwestern Perija, western Mara, southwestern Paez, and eastern Sucre in the State of Zulia. It is also exposed in the States of Lara and Falcon.

On the western side of Lake Maracaibo, the formations are carbonaceous, containing large amounts of coal, and are usually unaltered. On the eastern side of the lake they contain little coal, are darker in color, and in most places have been altered to quartzites and slates.

In the State of Falcon, a dark shale is predominant, with quartzitic sandstones and fossiliferous limestones interbedded. In eastern Venezuela, Eocene rocks are exposed on the west, southwest, and a part of the southern flank of the Cretaceous mountains. Alteration is less pronounced than in Falcon and eastern Zulia but more so than in western Zulia.

The massive sandstone formation in the upper part of the Eocene is easily recognized over much of northern Venezuela.

Probably a small amount of oil is indigenous to the shales and limestones of the Eocene. Large production should be obtained from the Eocene in localities where the sandstones are not quartzitic and have retained their porosity. Lying as it does immediately above the petroliferous upper member of the Cretaceous, it gives promise of being one of the principal oil horizons of Venezuela.

Oligocene.—In some localities where fossils are not found, rocks whose age is not definitely determined, have been classified as Oligocene because of their stratigraphic position. The rocks of the Oligocene are not exposed over any large area but are found on the east and west sides of the Maracaibo basin, in the State of Falcon, and in the State of Anzoategui.

There is a small angular unconformity between the rocks of this series and those of the underlying Eocene.

In western Zulia, the Oligocene is made up of dark brown, carbonaceous shale, sandy shale and thin-bedded sandstones about 2000 ft. in thickness.

In eastern Zulia, it is a dark gray shale commonly showing conchoidal fracture and containing iron-oxide concretions. In some localities, it contains thick lenses of foraminiferal limestones. It is about 3000 ft. thick.

In the State of Falcon, the shales have been altered so that they have a slaty appearance. In addition to the thick limestone lenses common in the Oligocene of eastern Zulia, the series here contains thin, black limestone beds. Its thickness is approximately 2000 ft.

In of Anzoategui, the series consists of massive, gray to brown sandstone beds in a thickly bedded fossiliferous, gray shale with iron-oxide concretions. Its thickness is about 1000 ft. In Zulia and Anzoategui, the sandstones and sandy shales provide good reservoirs for oil.

In eastern Zulia and Falcon, a small amount of high-gravity oil may be indigenous to the dark gray shale and limestone series.

Miocene.—While the angular unconformity between the Oligocene and Miocene is small, there is, in most localities, a pronounced change in the character of the rocks.

Exposures of rocks of Miocene age are widespread. The sediments were deposited under rapidly changing water conditions and the resultant rocks vary greatly in character and in thickness from place to place. There are few fossiliferous horizons in the Miocene of Zulia.

In both western and eastern Zulia, the Miocene is made up of a series of alternating beds of clays and sandstones with a thickness of 5000 to 8000 ft. The clays are soft and mottled white to red. The standstones are massive, friable, poorly sorted, coarse, and lenticular. The best exposures are found in the savannas east of the mountains in northern Perija. In southern Zulia, the Miocene is subject to greater variation in character and continuity. The deposits here are generally micaceous.

The State of Falcon offers the best area for the study of the Miocene, as it is exposed over most of the north-central portion of the state. Its thickness has been estimated at 15,000 ft. but as this is the summation of a series of measurements it doubtless involves overlap and the maximum thickness in any one place is probably considerably less. The formations show great lateral variation and the sandstones, especially, are lenticular. In Falcon, the lower part is generally made up of well-bedded, dark brown shales, locally containing lignite and well bedded, brown sandstones. In western Falcon, the upper part of the Miocene is very similar to the lower Miocene, with the shales much lighter in color. South of Coro, in north-central Falcon, the light-colored upper Miocene shales are interbedded with numerous fossiliferous, brown limestones.

In Zulia and Falcon, the Miocene rocks do not carry an abundance of bituminous material and therefore are probably not an original source of oil. There are, however, many excellent reservoirs in the soft, porous sands from some of which production is obtained at Mene Grande and El Mene.

In eastern Venezuela, the Miocene is composed of an alternating series of sandstones and shales. The shales are brown and fairly well laminated. The sandstones are brown, friable, and thin to thick bedded. The estimated thickness of the series is 1500 to 2500 ft. It is exposed in the foothills and near the mountains in the northeastern part of Anzoategui and northwestern Monagas.

Pliocene.—In north-central Anzoategui, a formation about 400 ft. thick lies unconformably over the older Miocene rocks. It is composed of light-colored clays and shales, poorly consolidated brown sandstones, a very few fossiliferous limestone beds and some lignites. On the basis of its fossils the formation is correlated as Pliocene or uppermost Miocene.

Quaternary

The major part of the southern portion of eastern Venezuela, north of the Orinoco River, is covered by rocks of the Quaternary system, termed the Llanos formation. It is composed of alternating beds of highly colored and mottled clays, massive sandstones and poorly sorted conglomerates. Its thickness is estimated at 250 feet.

A similar formation is exposed over much of the area in the northern part of the Maracaibo basin. Recent alluvials are deposited over large areas in the southern part of the Maracaibo basin and in the delta of the Orinoco River.

The Quaternary rocks, while unimportant in relation to petroleum, are a great handicap in the study of the more important underlying formations.

Historical Geology

A discussion of pre-Cretaceous history would have little bearing on the oil geology of Venezuela. During early Cretaceous time, much of northern South America was probably covered by a great epicontinental sea. The period was characterized by the deposition of great thicknesses of limestone over wide areas. This was followed by a gradual emergence and folding along the axes of the present mountain ranges so that the Maracaibo basin became separated from the sea covering eastern Venezuela. This emergence and relative elevation continued through the Eocene and Miocene periods. The newly exposed highlands were a source of detritus, which made up the Tertiary sediments. The progressive elevation of the mountain areas and the accumulation of sediments within the basins constantly restricted the area of sedimentation and the Cretaceous and Tertiary formations were successively exposed to erosion along the flanks of the uplift. Elevation and subsidence relative to sea level doubtless recurred from time to time, giving rise to overlap and to the minor unconformities noted in the Tertiary rocks.

The close of the Miocene period was marked by pronounced deformations and locally the Eocene and Oligocene shales and sandstones were metamorphosed to slates and quartzites. Since the close of Miocene time, conditions have been relatively quiescent although there have been periods of subsidence and elevation accompanied by some minor folding.

Structural Geology

The pre-Cretaceous rocks have been subjected to profound metamorphism but the resulting complicated structure has no bearing on the localization of oil. The major folding and faulting that culminated at the close of Miocene time resulted in the formation of the Llanos basin of eastern Venezuela and the geosyncline that includes the Maracaibo basin and the State of Falcon. Within these major areas, important folds and

faults were developed. For the most part, these are roughly parallel to the mountain ranges but many smaller folds and faults are at diverse angles.

The anticlines are commonly long with fairly straight axes and steeply dipping flanks. The faults are predominantly normal with displacement ranging from a few feet up to several thousand feet; as in the Toas and Petroleo faults in which the Cretaceous is brought into contact with Upper Tertiary beds.

Occurrence of Oil

Seepages

Very impressive seepages of oil and asphalt are found in many localities in Venezuela. They are distributed over a wide area and emanate from many different horizons. They vary from dry asphalt to oil of 30° Baumé.

The largest seepage in the world is Bermudez Lake at Guanoco, in eastern Venezuela. Numerous other seepages of heavy oil are found along a line extending west from Guanoco at the southern edge of the mountains. These seepages come from the Cretaceous shale. Eight miles south of this line is a seepage at Chapapotal, coming from the Quaternary, but with the Cretaceous shale undoubtedly very close to the surface. Still farther south, near Maturin, is a conspicuous line of seepages extending slightly south of west from the southern part of Trinidad and continuing west of Maturin. These seepages also issue from the Quaternary but evidence on Trinidad indicates that a Miocene petroliferous horizon is near the surface.

In western Venezuela seepages are numerous. There are many in western Zulia along the Inciarte, Petroleo, La Luna fault zone. Most of these give heavy oil and the one at Inciarte is a large asphalt lake. In the district of Colon and in the highly folded Eocene formations along the south and southeastern edges of the Maracaibo basin are many seepages of light oil.

At Mene Grande, there are hundreds of seepages covering about 1 sq. mi. and issuing from the Upper Eocene and Upper Miocene rocks. At El Mene, in Falcon, is a seepage of light oil from Upper Miocene rocks. There are many small seepages from the Miocene in western Falcon.

Producing Wells

Oil in commercial quantities has been found in rocks ranging, in age, from Eocene to Upper Miocene. The wells in the Rio de Oro and Rio Tarra fields in Colon are in the Eocene. The wells in the Menito (Misoa) field are in the Oligocene. The wells in the Mene Grande, La Rosa, La Paz, El Mene, and Petroleo fields are in the Middle or Upper Miocene.

Résumé

1. Oil has been found in many sands in formations ranging in age from the Cretaceous to the Quaternary.

2. So far as the geology has been worked out in the producing fields, the producing horizon has been folded into anticlines with steeply dipping flanks, as in Colon and at El Mene and Misoa. It appears, therefore, that anticlines are a requisite for oil production.

3. Oil is indigenous to the upper Cretaceous shales wherever this formation has been deposited. Some oil has had its origin, also, in the dark carbonaceous shales and limestones in the lower part of the Eocene; and a smaller amount in the Oligocene shales and limestones of Falcon and eastern Zulia.

4. These horizons may have contributed oil to the overlying porous beds until the close of the Miocene period, after which they were altered locally, and in such localities were no longer available as a source of oil. This alteration is least in the western part of the Maracaibo basin and along the southern edge of the mountains in eastern Venezuela.

5. The great diastrophic activity at the close of Miocene time permitted relatively rapid migration of oil into the overlying beds along the fractures and fault zones formed at that time.

6. A considerable amount of oil has accumulated along the zones of major faulting but the greatest quantities are retained in steep sided anticlines in which the folding has been accompanied by fracturing or faulting.

7. The producing sands, especially in the later formations, are lenticular and in many of the fields production will be spotted.

8. Sand and sandstone beds will be the producing formations. The degree of alteration and the resultant porosity of these beds is an important guide to localities of oil accumulation.

9. The numerous porous sandstones interbedded with impervious shales and clays afford an abundance of reservoirs for the accumulation of oil in the post-Cretaceous rocks. Production may be obtained from any of these sands, dependent on the porosity of the sands, the extent of fracturing or faulting of the underlying formations and the presence of suitable structure.

BIOGRAPHIES

David Talbot Day

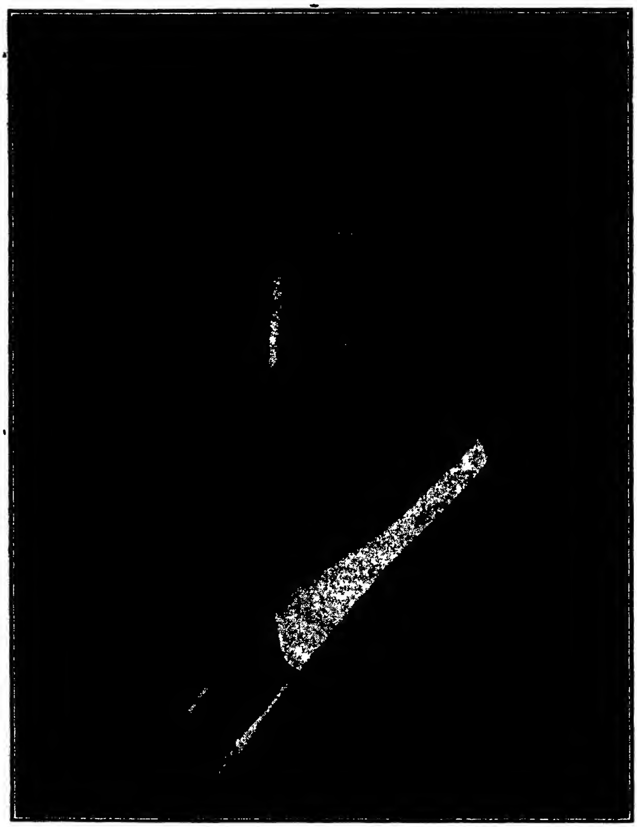
DAVID TALBOT DAY, a member of the Institute since 1887 and its vice-president in 1893 and 1900, passed away suddenly at the home of a friend in Washington, D. C., on April 15, 1925. The son of Willard Gibson and Caroline Cathcart Day, he was born at Lakewood, Ohio, on Sept. 10, 1859. He received his collegiate training at Johns Hopkins University, Baltimore, Md., taking an A. B. degree in 1881 and a Ph. D. degree in 1884, in the same class as President Wilson. He served for two years as demonstrator of chemistry in the University of Maryland, and in 1886 married Elizabeth Eliot Keeler, of Mayport, Fla. Soon after this marraige, Doctor Day went to Washington, D. C., and was chosen by Albert Williams, Jr., as his successor in the statistical work of the United States Geological Survey.

Doctor Day was connected with the Geological Survey for 28 years, and from 1886 to 1907 he was in charge of the Mineral Resources division. To his organizing genius and his ability to meet men in all walks of life and to convince them of the sincerity of his purpose, is to be credited most of the progress made in twenty years in the establishment of the series of reports containing the annual statistics of mineral production and the rapid development of the mineral industry of the United States. In building up a strong organization for the collection of mineral statistics, Doctor Day was ably seconded by Edward W. Parker, who stood in the same relation to the coal industry that Doctor Day stood to the mineral industry as a whole, and the hearty coöperation of the two men achieved a result that has been of lasting benefit to the Geological Survey and to the business interests of the country.

Doctor Day was, by choice and training, a chemist, and from the time he left the university he evinced great interest in the chemistry and technology of petroleum. Several papers on this subject were published by him during his connection with the Geological Survey, but an industry that was already established did not hold for him the attraction of one that was in the formative stage and was struggling for existence. Accordingly, in the height of the rapid development of the oil industry of the United States, Doctor Day turned his attention largely to the problem of the utilization of oil shale. He resigned his position as chief of the Division of Mineral Resources of the Geological Survey in 1907 and became consulting chemist, mainly in the line of oil-shale investigations.

Doctor Day was indomitably optimistic regarding the establishment in this country of an oil-shale industry, and, in association with E. G.

Woodruff, and under the auspices of the Geological Survey, made the first survey and field tests of the great oil-shale beds of northwestern Colorado and northeastern Utah. The part played by Doctor Day in the establishment of the naval petroleum and oil-shale reserves constitutes, perhaps, his greatest service to the American public. It was under the stimulus of his optimistic belief in the ultimate value and importance of oil shale as a source of future supplies for the United



David T. Day.

States that the Geological Survey mapped and critically studied all of the more important oil-shale fields of this country. As his chosen field of operations was more closely related to the technology of oil shale than to its geology, he resigned from the Geological Survey in 1914 and was appointed consulting chemist of the Bureau of Mines. In 1920, he severed his connection with the Government service so that he might have a free hand in carrying out experimental work on the distillation of oil shale with the hope of ultimately establishing a new industry on this great undeveloped resource of the country.

As many of his problems could best be solved in the West, Doctor Day moved to Santa Maria, Calif., within easy reach of the oil fields and also of large deposits of oil shale. He erected there a plant for distilling oil shale and conducted an elaborate series of experiments which confirmed his belief that this shale could be utilized in a commercial way for the production of gasoline and the various byproducts incidental to that operation.

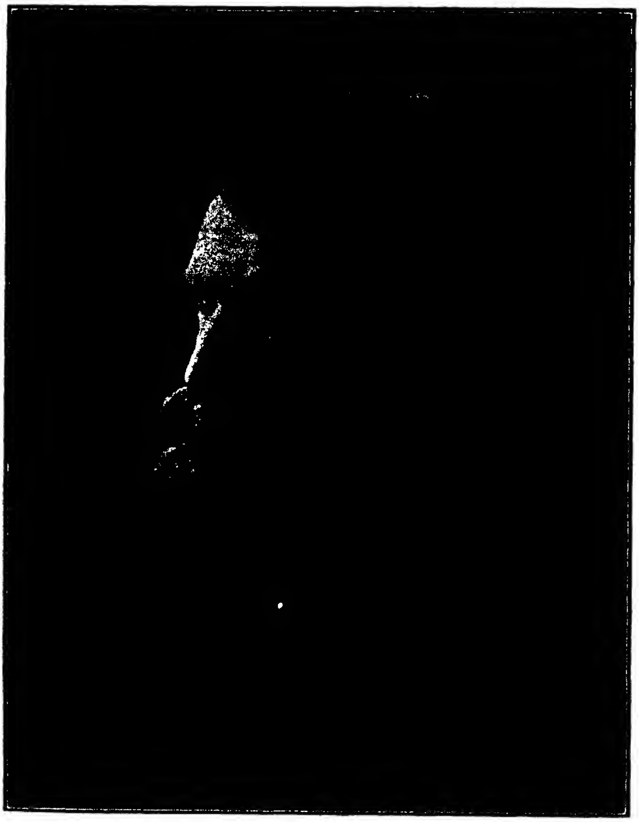
Despite the large amount of time consumed in his experimental work and in serving as consulting chemist and geologist for large oil companies, he found time to plan a Handbook of the Petroleum Industry and direct its compilation. This was published in 1922 in two volumes and has become a standard reference book for those interested in the many branches of the petroleum industry.

Doctor Day is survived by his wife, a daughter, Mrs. Stanley G. Breneizer of Santa Maria, Calif.; a son, David Eliot Day, a petroleum engineer in Los Angeles; and by a host of friends who were attracted to him by his loving disposition which found good in all mankind.

M. R. Campbell.

William A. Clark

WILLIAM ANDREWS CLARK, former United States senator from Montana, died at his home in New York on March 2, at the age of 86, after a brief illness due to pneumonia. He was the last of the three great Montana mining magnates, Clark, Daly and Heinze.



WILLIAM A. CLARK.

He was born in Connellsville, Pa., on Jan. 8, 1839, and in 1863 arrived in Bannock, Ida., with only five dollars, after a journey of 65 days. On reaching Idaho, he became successively a miner, teamster, machinist, railway builder, mine owner, capitalist and, in his more recent years, philanthropist and art collector.

He accumulated his first thousand dollars sluicing gold on a placer claim on Horse Prairie, Ida. He bought a mule team, traveled to Salt Lake and freighted provisions back to the miners. In 1867 he took a government contract to carry mail from Missoula, Mont., to Walla Walla, Wash., and on two occasions made the greater part of the journey on snowshoes.

When teaching school, he studied law, and later entered Mount Pleasant University in Idaho, but he never entered the bar.

At the age of 33, he purchased an interest in some of the principal claims in Butte and four years later built the first silver stamp mill in that camp, making it the greatest silver producer in America. Then he became a copper king and 35 years later helped to make Butte one of the most important zinc camps. He financed and owned more than 50 per cent. of the stock of the San Pedro, Los Angeles and Salt Lake Railroad. Just after the road was completed, floods washed out great sections of it, causing a loss of $16,000,000; for the second time he poured his wealth into the reconstruction of this road.

During the Nez Perce Indian uprising in 1868, he organized a battalion of engineers and, as its major, helped quell the trouble.

He became almost the sole owner of the United Verde Copper Co., at Jerome, Ariz. He regarded it as strictly a personal affair and less is known of it, by the profession, than of any other of the large copper producers.

He maintained two palatial residences, one in New York, and one in Butte. In his later years, he was much interested in art and had in his New York galleries the largest individual collection of Corots in the world. He devoted millions of dollars to philanthropy, about which little is known.

Although, in the later years of his life, he devoted much time to travel, social intercourse, collecting and philanthropy, he maintained close contact with the most intimate details of his mining operations.

His passing marks the end of a generation famous for picturesque characters in the mining world, among whom he stood pre-eminent.

Willet G. Miller

The mining fraternity of North America was grieved and shocked to learn of the death of Dr. Willet G. Miller on Feb. 10, 1925. Doctor Miller was for many years the Provincial Geologist of Ontario and the one who more than any other had contributed by his personal work and the reports of his subordinates to the recent extraordinary mineral development of the Province.

Doctor Miller was fifty-eight at the time of his decease. A man of unusually stalwart physique, he seemed destined to many years of useful service. His friends in both the American and Canadian Mining Institutes can with difficulty reconcile themselves to his loss.

Doctor Miller was born in 1867 in Port Rowan, Ont., on the shores of Lake Erie. After preparation in the high school of his native town, he entered the University of Toronto and took his bachelor's degree in 1890. He pursued graduate studies in geology at Chicago, Harvard, and Heidelberg Universities. In 1893, he was first appointed lecturer and soon thereafter Professor of Geology in Queens University, Kingston, Ont., a chair which he held until 1902. He was then appointed Provincial Geologist of Ontario and was placed at the head of the Survey which was attached to the Department of Mines. Within the next year, 1903, he performed the service that made him famous.

In the summer of 1903, in connection with the building of the Ontario Government Railway toward an objective on James Bay, veins had been noticed by construction parties just north of what is Cobalt Lake today, and in the rocky pass that is now traversed by the main line of the Canadian National Railway en route to Vancouver. The pink stain of cobalt bloom on the vein, known later as La Rose, caught the eye of a workman; in November, Doctor Miller recognized the silver in it, and brought the possibilities of the district to general attention. In December, he published an article in the *Engineering and Mining Journal*, stating that the veins could be worked at a handsome profit. During the winter and spring, the mining interest awoke, which resulted in the astonishingly productive silver district of Cobalt; but in which, Doctor Miller, because a government official, scrupulously refrained from having any financial interest whatever. Seldom has so high a sense of honor been manifested; and as the result, Doctor Miller commanded confidence and respect to an extraordinary degree. Hard on the discoveries at Cobalt came, in the next few years, those at the other famous camps in Northern Ontario; and step by step with them, reports issued from

the office of the Provincial Geologist, which assisted in their intelligent development.

Doctor Miller was Councilor of the American Institute of Mining Engineers 1909–1911, and Director 1917–1919. In the Canadian Mining Institute, he served as President 1908–1910. In the Geological Society of America, he was Vice-President in 1920. He was an Honorary Member of the Institution of Mining and Metallurgy of London, and received the gold medal in 1913. Queens University conferred upon him the honorary degree of LL.D. in 1907, and at a special convocation which was one of the features of the International Geological Congress, in Toronto, 1913, his alma mater also conferred upon him the honorary degree of LL.D.

Doctor Miller was one whose simple and unaffected manner reflected the directness and sterling honesty of his character. He was a geologist of marked and outstanding ability, and in addition to his contributions on mining, investigated of the ancient geological formations of the North.

His loss will be profoundly felt on both sides of the international boundary, and for his great services, the Board of Directors of the American Institute of Mining and Metallurgical Engineers desire, to record this memorial of appreciation and respect.

The Board of Directors at its February Meeting ordered this memorial to be spread upon its minutes, and to be sent to his family with an expression of deep sympathy in their loss.

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[Note.—In this Index, the names of the authors of papers are printed in SMALL CAPITALS, and the titles of papers in *italics*.]